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One-pot synthesis of *trans*-β-alkylstyrenes

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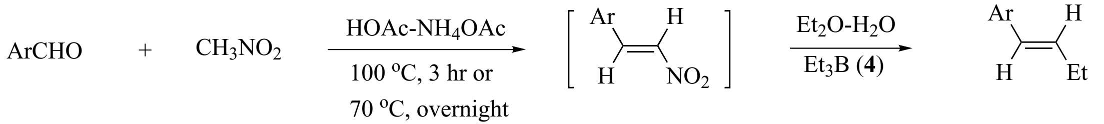
Abstract—One-pot synthesis of (*E*)-alkenes **5** from the reactions of aldehyde **1** and nitromethane **2** in the acetic acid solution and then with triethylborane **4** in the biphase of diethyl ether and aqueous solution in the presence of oxygen in air was reported. Various (*E*)-alkenes **7** could also be prepared when different kinds of secondary or tertiary alkyl iodides **6** were used under similar conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Nitro olefins are useful intermediates in organic synthesis and can be used as starting materials for many classes of compounds.[1] Reactions of β-nitrostyrenes with dialkylzinc or organozinc halides,[2] *t*-BuHgX/KI,[3] organomanganese,[4] trialkylgallium,[5] organoborane,[6] triethylaluminum or diethylaluminum chloride,[7] and Grignard reagents,[8] respectively, to generate alkenes and/or nitroalkanes or halooximes have been reported. These results indicate that β-nitrostyrenes can react with different organometallic reagents to generate different products under different conditions and workup procedures and the reaction mechanism is proposed to be free-radical and/or an ionic reaction.[1–8]

The Knoevenagel condensation reaction of carbonyl compounds with nitroalkanes as the methylene component (Henry reaction) is a general and useful method for the preparation of nitroaldols or nitroalkenes.[9] It has been reported that 35–90% of nitroalkenes may be isolated when different aromatic aldehydes react with the appropriate nitroalkanes in an acetic acid solution with ammonium acetate at 100°C for a few hours.[10]

Triethylborane[11,12] and diethylzinc[2a,12d–e,13] not only can be served as one of the methods for the generation of radical species but also can be used as an effective radical initiator to generate different radicals by reaction of triethylborane or diethylzinc with alkyl halides in the presence of tin hydride under mild conditions. On the basis of literature reports, we wish to report an easy and effective method to synthesize different (*E*)-alkenes in one-pot condition by combining our previous study[6] and literature methodology.[11–13] The strategy is to react β-nitrostyrenes **3**, in situ prepared from aromatic aldehydes **1** with nitromethane **2** in the acetic acid solution with a catalytic amount of ammonium acetate at 100°C for 3 hours (method A)[10] or at 70°C for overnight (method B), with triethylborane **4** in the biphase of diethyl ether and aqueous solution in the presence of oxygen in air as radical initiator at room temperature for 5–10 minutes to generate **5** (Eq. (1)).



(1)

1 **2** **3** **5**

Benzaldehyde **1a** (1 mmol) reacted with nitromethane **2** (1 mL) in the acetic acid solution (1 mL) with ammonium acetate (0.1 mmol) at 100°C for 3 hours (method A)[10] to generate 98% of NMR (93% of isolated) yield of (*E*)-β-nitrostyrene **3a**. When triethylborane **4** (4 mmol in hexane) was dropwise added into the acetic acid and nitromethane solution in the presence of oxygen in air as radical initiator at room temperature for 5–10 minutes, 21% of (*E*)-1-phenylbutene **5a** and 76% of (*E*)-β-nitrostyrene **3a** (NMR yield) were observed after the solution was quenched with water and extracted with diethyl ether (entry 1 of Table 1). Similarly, when 10 mL of diethyl ether was added into the acetic acid and nitromethane solution to form the homogeneous solution and then the mixture was added triethylborane, 46% of **5a** and 50% of **3a** were observed (entry 2 of Table 1). We were also surprised to find that both 43%

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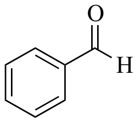

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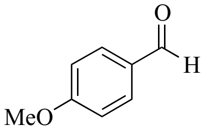

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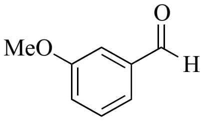

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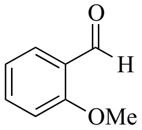

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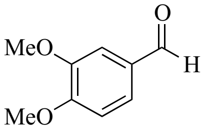

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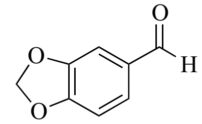

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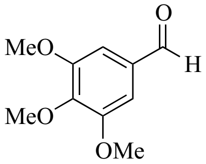

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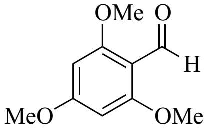

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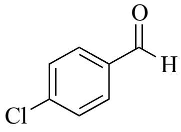

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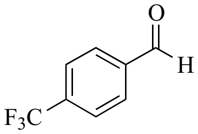

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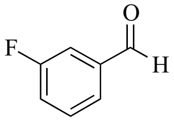

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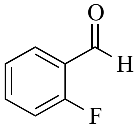

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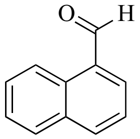

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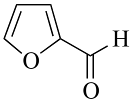

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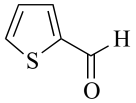


Table 1. One-pot synthesis of *trans*-alkenes **5** from aromatic aldehyde **1**, nitromethane **2**, and triethylborane **4**

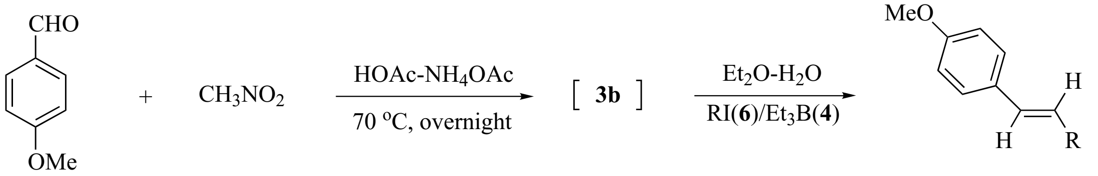
Entry	Substrate	Method	Product	NMR yield (%)	Isolated yield (%)
1	**1a**	A	**5a**	21[a]	–
2	**1a**	A	**5a**	46[b]	–
3	**1a**	A	**5a**	43[c]	–
4	**1a**	A	**5a**	94	79
5	**1b**	A	**5b**	71[d]	–
6	**1b**	B	**5b**	90	79
7	**1c**	B	**5c**	90	81
8	**1d**	B	**5d**	88	78
9	**1e**	B	**5e**	75	66
10	**1f**	B	**5f**	78	68
11	**1g**	B	**5g**	96	85
12	**1h**	B	**5h**	87	79
13	**1i**	A	**5i**	77	65
14	**1i**	B	**5i**	76	–
15	**1j**	A	**5j**	72	62
16	**1k**	A	**5k**	76	61
17	**1k**	B	**5k**	64	–
18	**1l**	A	**5l**	96	83
19	**1l**	B	**5l**	65	–
20	**1m**	A	**5m**	82	–
21	**1m**	B	**5m**	83	75
22	**1n**	A	**5n**	70	51
23	**1n**	B	**5n**	51	–
24	**1o**	A	**5o**	51	–
25	**1o**	B	**5o**	69	55

[a] 76% of **3a**.
[b] 50% of **3a**.
[c] 53% of **3a**.
[d] 26% of **1b**.

of **5a** and 53% of **3a** were also observed when 4 mL of water were added into the acetic acid solution and then to the mixture was added triethylborane and worked up as described above (entry 3 of Table 1). This result indicates that the free radical reaction also occurred in the aqueous solution. On the basis of the results of entries 1–3, we first tried to add 10 mL of diethyl ether to form a homogenous solution and then add 4 mL of water to form the biphase of diethyl ether and aqueous solution and then the triethylborane was added dropwise, as described above. Surprisingly, only 94% of **5a** and traces of unidentified products were observed under these conditions (entry 4 of Table 1). When the crude mixture was checked by NMR or analyzed by GCMS, no **3a** was detected in the solution. This result indicates that **3a** has reacted with triethylborane[6] completely under these conditions and the purification of **3a** is not necessary during the reaction because the solvent, such as acetic acid, and the catalyst, such as ammonium acetate, and other water soluble compounds have dissolved in the aqueous solution and have no effect on the free radical reaction which occurs in the diethyl ether solution. This is an easy and effective method to prepare **5a** from **1a** and **2** to generate **3a** and then react with **4** in a one-pot reaction, and this method can also be applied to prepare other *trans*-alkenes **5** just by using different kinds of aromatic aldehydes **1**.

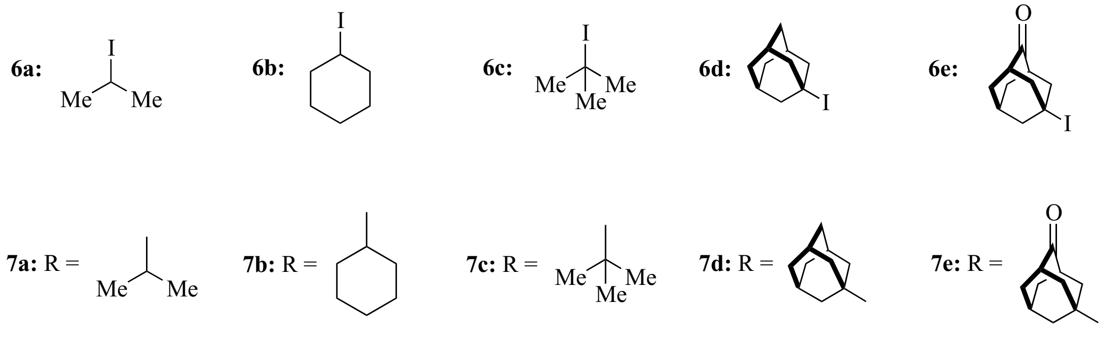
With electron-donating substituted aldehyde **1b** and by using method A, not only 71% of **5b** but also 26% of unreacted **1b** was also observed in the crude NMR analysis (entry 5 of Table 1). This result is also consistent with the literature report that the condensation of electron rich aromatic aldehyde with nitroalkanes always affords low yield of nitroalkenes.[14] To improve the yield of **5b**, the reaction temperature was decreased from 100 to 70°C and the reaction time was increased from 3 hours to overnight (method B) and then the solution was treated with triethylborane in the biphase of diethyl ether and an aqueous solution, as described above. A higher yield (90%) of **5b** and only a trace of unreacted starting material **1b** were observed in the crude NMR analysis (entry 6 of Table 1). With electron-withdrawing substituted aldehyde **1l** and by using method A, 96% of **5l** was generated (entry 18 of Table 1) and only 65% of **5l** was observed by using method B (entry 19 of Table 1) and these results indicate that the electron-withdrawing group can accelerate the generation of the intermediate **3** dramatically so that only 3 hours are long enough for these reactions. With other aromatic aldehydes **1**, medium to high yields of **5** were also observed; all the experimental data are shown in Table 1.

Tashtoush and Sustmann reported that alkyl radicals including 1-adamantyl radical and aryl radical can be generated by the reduction of alkyl or aryl halides with (ethylenediamine)chromium(II) complexes in dry dimethylformamide.[15] Bräse et al. also reported that the palladium-catalyzed reaction of 1-bromoadamantane with styrene and donor-substituted styrenes give 15–41% of the corresponding Heck-type coupling product



1b **2** **7** (2)

Table 2. One-pot synthesis of *trans*-alkenes **5** from aromatic aldehyde **1**, nitromethane **2**, alkyl iodide **6**, and triethylborane **4**



Entry	Substrate	Method	RI	Product	NMR yield (%)	Isolated yield (%)
1	**1b**	B	**6a**	**7a**	88	73
2	**1b**	B	**6b**	**7b**	73	65
3	**1b**	B	**6c**	**7c**	70	61
4	**1b**	B	**6d**	**7d**	76	65
5	**1b**	B	**6d**	**7e**	84	74

(*E*)-1-adamantyl-2-arylethene.[16] Similarly, Yamataka and co-workers have also reported that both (*Z*)- and (*E*)-1-adamantyl-2-arylethene mixture can be prepared from the Wittig reaction of substituted benzaldehydes with (1-adamantylmethylidene)triphenylphosphorane.[17] Our recent study also found that similar products can also be prepared from the reaction of **1b** with iodoadamantane or 5-iodoadamantan-2-one and triethylaluminum in the presence of benzoyl peroxide.[18]

After observation of the literature reports, we tried to apply this methodology to react **1b** with different radicals generated from alkyl iodide **6** (6–20 equivalents) and **4** (4 equivalents), under similar conditions, to prepare other alkenes (Eq. (2)). As expected, medium to high yields of **7** were generated under similar procedures and conditions as described above (Table 2). This result indicates that not only the ethyl radical but also the different secondary or tertiary radical can react with **1** to obtain different *trans*-alkenes **7**.

In conclusion, we have developed an easy and effective method to prepare medium to high yields of (*E*)-alkenes by using aromatic aldehydes, nitromethane, alkyl iodide RI, and triethylborane in the biphase solution of diethyl ether and aqueous solution in one-pot condition in the presence of oxygen in air. Further study about the application of this methodology to synthesize other compounds is under investigation.

Acknowledgements

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