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Novel synthesis of alkenes via triethylaluminum-induced free radical reactions of alkyl iodides and β-nitrostyrenes

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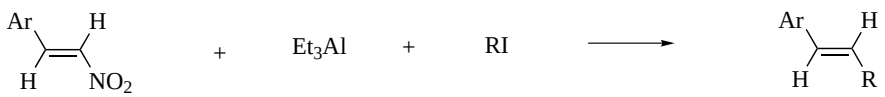
Abstract—Reactions of (*E*)-β-nitrostyrenes **1** with triethylaluminum (Et_3Al) **2** and alkyl iodide (RI) **3**, **4**, or **5** in the presence of benzoyl peroxide in diethyl ether solution at room temperature to give 60–100% of the different (*E*)-alkenes **6**, **7**, or **8**. Under similar conditions, 95% of 1-adamantyl-2-(4-methoxyphenyl)ethene **10** or 80% of 1-(4-oxoadamantyl)-2-(4-methoxyphenyl)ethene **12** also can be easily prepared by using 1-iodoadamantane **9** or 5-iodo-2-adamantanone **11** and **2**.

Nitro olefins are useful intermediates in organic synthesis and are important structural units which 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] and Grignard reagents,[7] respectively, to generate alkenes and/or nitroalkanes or halooximes have been reported. All 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 a free radical and/or an ionic reaction.[1–7]

Reactions of trialkylaluminum or triorganoaluminum–ether complexes with α,β-unsaturated nitroalkenes to generate high yields of 1,4-alkylated products have been reported by Pecunioso and Menicagli.[8] Our previous study also found that medium to high yields of alkenes and/or hydroximoyl chloride can be generated when (*E*)-β-nitrostyrenes **1** reacts with triethylaluminum or diethylaluminum chloride in a diethyl ether solution under refluxing conditions in the presence of a trace of oxygen in the nitrogen or by photolysis in the presence of benzoyl peroxide as a radical initiator or in the presence of $MgCl_2$ as the Lewis acid after the solution was worked-up with ice-cold concentrated hydrochloric



1 **2** **3, 4, 5** **6, 7, 8** (1)

6	**7**	**8**
a: Ar = Ph, R = *i*-Pr	**a:** Ar = Ph, R = *c*-C_6H_{11}	**a:** Ar = Ph, R = *t*-Bu
b: Ar = 4-$MeOC_6H_4$, R = *i*-Pr	**b:** Ar = 4-$MeOC_6H_4$, R = *c*-C_6H_{11}	**b:** Ar = 4-$MeOC_6H_4$, R = *t*-Bu
c: Ar = 4-ClC_6H_4, R = *i*-Pr	**c:** Ar = 4-ClC_6H_4, R = *c*-C_6H_{11}	**c:** Ar = 4-ClC_6H_4, R = *t*-Bu
d: Ar = 2-thienyl, R = *i*-Pr	**d:** Ar = 2-thienyl, R = *c*-C_6H_{11}	**d:** Ar = 2-thienyl, R = *t*-Bu
e: Ar = 2-furyl, R = *i*-Pr	**e:** Ar = 2-furyl, R = *c*-C_6H_{11}	**e:** Ar = 2-furyl, R = *t*-Bu

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acid.[9a] The mechanism of the generation of the alkenes is proposed to be free radical substitution[1–6] and the generation of the hydroximoyl chloride is proposed to be ionic reaction that is similar to literature proposed.[7,8]

Triethylborane[10,11] and diethylzinc[2a,11d,e,12] 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,[9] we wish to report an effective method by combining our previous study[9a] and the literature method,[9b] to synthesize different alkenes by reaction of β-nitrostyrenes with different radicals, prepared from alkyl iodides and triethylaluminum in the presence of benzoyl peroxide as a radical initiator, in diethyl ether solution at room temperature.

At room temperature, (*E*)-β-nitrostyrenes **1a–e** (**a**: Ar = Ph, **b**: Ar = 4-$MeOC_6H_4$, **c**: Ar = 4-ClC_6H_4, **d**: Ar = 2-thienyl, **e**: Ar = 2-furyl) reacted with triethylaluminum **2** and alkyl iodides RI such as isopropyl iodide **3**, cyclohexyl iodide **4**, or *tert*-butyl iodide **5** in diethyl ether solution in the presence of benzoyl peroxide at room temperature to generate 60–100% of 1-aryl-2-alkylethenes **6**, **7**, or **8** within 1.5–2 h (Eq. (1) and Table 1). All spectral data indicate that the alkenes have (*E*) configuration (J_{trans} = 16.0–16.2 Hz for vinyl hydrogen) after the mixture was purified by flash column chromatography and most of the spectral data of the known products are also consistent with literature reports.[2,8] Gas chromatography and proton NMR analysis of the crude mixture also found that only the (*E*) isomer and none of the (*Z*) isomer could be detected.

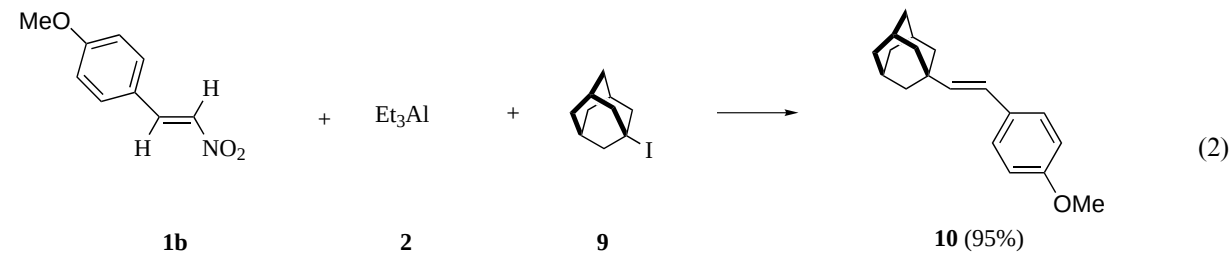
Tashtoush and Sustmann have reported that alkyl radicals including 1-adamantyl radical and aryl radical can be generated by the reduction of alkyl or aryl halides with (ethylenediamine)chromium(II) complexes in dry dimethylformamide.[13] Bräse et al. also have reported the palladium–catalyzed reaction of 1-bromoadamantane with styrene and donor-substituted styrenes give the corresponding Heck-type coupling product (*E*)-1-adamantyl-2-arylethene in 15–41%.[14] Similarly, Yamataka and coworkers 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.[15] After observation of Eq. (1) and Table 1, we applied this method to prepare similar product by reaction of **1b** with 1-iodoadamantane **9** and **2** under similar conditions. To our surprise, not only high yields (95%) of the expected products 1-adamantyl-2-(4-methoxyphenyl)arylethene **10** but also only the *trans* isomer was generated at room temperature (Eq. (2)). This result indicates that adamantyl radical can also be generated by using **9** and **2** at room temperature in the presence of benzoyl peroxide. Similarly, **12** can also be isolated in 80% yield when 5-iodo-2-adamantone **11** was reacted with **1b** and **2** under similar conditions (Eq. (3)).

Table 1. Reaction of (*E*)-β-nitrostyrenes **1** (1 equiv.) with RI (6–20 equiv.), Et_3Al (2–6 equiv.), and benzoyl peroxide (2 equiv.) in diethyl ether at room temperature

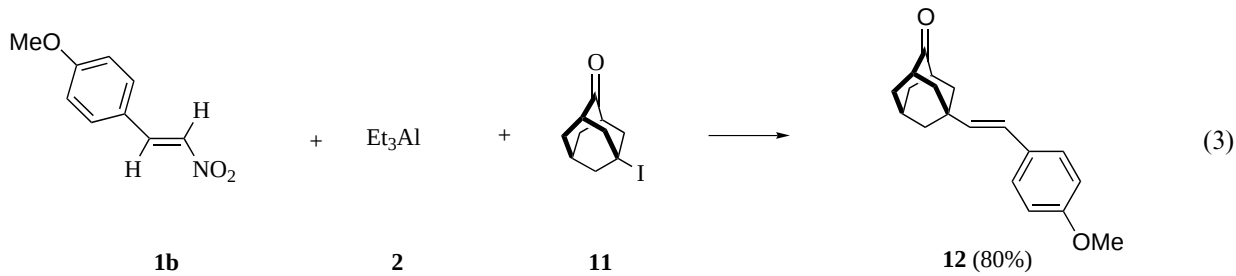
Entry	1	RI (equiv.)	Product	Yield (%)[a]
1	**1a**	**3** (20)	**6a**	96
2	**1b**	**3** (20)	**6b**	99
3	**1c**	**3** (20)	**6c**	100
4	**1d**	**3** (20)	**6d**	98
5	**1e**	**3** (20)	**6e**	100
6	**1a**	**4** (20)	**7a**	99
7	**1b**	**4** (20)	**7b**	99
8	**1c**	**4** (20)	**7c**	97
9	**1d**	**4** (20)	**7d**	98
10	**1e**	**4** (20)	**7e**	90
11	**1a**	**5** (6)	**8a**	79
12	**1b**	**5** (6)	**8b**	72
13	**1c**	**5** (6)	**8c**	60
14	**1d**	**5** (6)	**8d**	77
15	**1e**	**5** (6)	**8e**	70

[a] NMR yields.

In conclusion, our study found that the triethylaluminum can serve as an initiator to induce radical



1b **2** **9** **10** (95%) (2)



1b **2** **11** **12** (80%) (3)

reactions to prepare (*E*)-alkenes by using (*E*)-β-nitrostyrenes, alkyl iodide RI, and triethylaluminum in the presence of benzoyl peroxide in diethyl ether solution at room temperature. Further study about the reaction mechanism and the application of this methodology to synthesize other compounds will be reported in the future.

Acknowledgements

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