This article was downloaded by: [Umeå University Library] On: 15 November 2014, At: 22:39 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/lsyc20

Conjugate Addition of Triallylaluminum to α,β-Unsaturated Nitroalkenes to Produce 4,5-Unsaturated Nitroalkenes

Kao-Hsien Shen^a, Ju-Tsung Liu^a, Yih-Ru Wu^a & Ching-Fa Yao^a ^a Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, China Published online: 05 Oct 2007.

To cite this article: Kao-Hsien Shen , Ju-Tsung Liu , Yih-Ru Wu & Ching-Fa Yao (2007) Conjugate Addition of Triallylaluminum to α,β-Unsaturated Nitroalkenes to Produce 4,5-Unsaturated Nitroalkenes, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:20, 3677-3687, DOI: 10.1080/00397910600978184

To link to this article: http://dx.doi.org/10.1080/00397910600978184

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthetic Communications[®], 37: 3677–3687, 2007 Copyright © Taylor & Francis Group, LLC ISSN 0039-7911 print/1532-2432 online DOI: 10.1080/00397910600978184



Conjugate Addition of Triallylaluminum to α,β-Unsaturated Nitroalkenes to Produce 4,5-Unsaturated Nitroalkenes

Kao-Hsien Shen, Ju-Tsung Liu, Yih-Ru Wu, and Ching-Fa Yao

Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan, China

Abstract: The reaction of aryl substituted α,β -unsaturated nitroalkenes **1a**-**g** with triallylaluminum **2** in ether solution at 0°C generated low to high yields of 4,5-unsaturated nitroalkenes **3a**-**g** after adding the nitronate to an ice-cold solution of dilute hydrobromic acid. The yields of products **3h**-**j** were increased substantially when the alkyl substituted α,β -unsaturated nitroalkenes **1i** and **1j** reacted with **2** in the presence of aluminum chloride. The most important thing is triallylaluminum was prepared from allyl bromide and pure elemental Al, not from Grignard reagent.

Keywords: conjugate addition, triallylaluminum, α,β -unsaturated nitroalkenes, 4,5-unsaturated nitroalkenes

INTRODUCTION

Nitroalkenes are one of the more useful intermediates in organic synthesis and can be used as starting materials for the synthesis of a variety of compounds.^[1] Reactions of nitroalkenes with allyl organometallic reagents such as allyl Grignard reagents,^[2] allylsamarium bromides,^[3] allylzinc reagents,^[4] allyltin and allylsilanes,^[5] or organoaluminum Et₂AlR₂MgX (R = allyl,

Received in R.O.C. March 12, 2006

Address correspondence to Ching-Fa Yao, Department of Chemistry, National Taiwan Normal University 88, Sec. 4, Tingchow Road, Taipei, Taiwan, China. E-mail: cheyaocf@scc.ntnu.edu.tw

phenyl, or benzyl)^[6] result in the formation of the 1,4-addition products, and the reaction mechanism was proposed to involve an ionic reaction.

Although the reaction of nitroalkene with allyl Grignard reagent in tetrahydrofuran (THF) at -78° C has been reported by Barboni et al. excellent yields were obtained only when an aromatic nucleus was present in the β -position; aliphatic substituent in that position, such as 1-nitrohex-1-ene or 1-nitrocyclohexene, leads to an intractable mixture.^[2] Similarly, reactions of α , β -unsaturated nitroalkenes in hexane solution with either trialkylaluminum R₃Al (R = Et or *i*-Bu) or a trialkylaluminum etherate R₃Al OEt₂ (R = Et, *i*-Bu or Ph)^[6a] at 0°C or a tetraorganoalanate such as [R₃AlR']M (R' = allyl or phenyl, M = MgX or Li) or [R₂AlR'₂]MgX (R' = allyl, phenyl, or benzyl)^[6b] to generate the conjugate addition products have also been reported by Pecunioso. However, surprisingly, only the unreacted nitroalkene was recovered when 1-nitrocyclohexene was reacted with triisobutylaluminum or diethylallylaluminum in diethyl ether.^[6b]

Our group also reported that the Michael addition of a Grignard or an organolithium reagent to β -nitrostyrenes generated high yields of nitroalkanes when the nitronate was added to an ice-cold and dilute hydrochloric acid solution.^[7a,b] Similarly, triethylaluminum or diethylaluminum chloride also reacts with β -nitrostyrenes in ether solution to generate chlorooximes and alkenes. The proposed reaction mechanism involves an ionic 1,4-conjugate addition to produce chlorooxime and the free-radical substitution of the nitro group to yield an alkene.^[7b]

We recently reported that triallylaluminum reacts with aldehydes, ketones, aldimines, and ketimines in excellent yields.^[8] Herein, we report on the allylation of α,β -unsaturated nitroalkene with triallylaluminum. To the best of our knowledge, reactions of the α,β -unsaturated nitroalkene **1** and triallylaluminum **2** have not been reported. Based on the previous study, we predict that triallylaluminum might function as an allyl organometallic reagent^[2–5] and that an organoaluminum reagent such as trialkylaluminum,^[6a,7a] dialkylaluminum chloride,^[7c] or triphenylaluminum^[6a] would react with α,β -unsaturated nitroalkenes to generate different products. The most significant feature of this reaction concerns the preparation of the triallylaluminum reagent, from allyl bromide and pure elemental Al,^[9,10] as opposed to earlier reports in which the allylaluminum was prepared from alkylaluminum and allylmagnesium.^[11]

RESULTS AND DISCUSSION

In general, the allylaluminum reagents were prepared by coupling commercially available aluminum chloride (Me₂AlCl) with the appropriate Grignard or organolithium reagent.^[10] In this article, the triallylaluminum reagent **2** was first prepared by reacting allyl bromide and elemental aluminum in ether under reflux conditions according to literature procedures (Scheme 1).^[9,10]

 $3 \text{ CH}_2=\text{CHCH}_2\text{Br} + 2 \text{ Al} \xrightarrow{\text{ether}} (\text{CH}_2=\text{CHCH}_2)_3\text{Al} + \text{AlBr}_3$ Scheme 1.



When triallylaluminum **2** was rapidly added to the β -nitrostyrene **1a** dissolved in ether solution at 0°C under nitrogen, the yellow color of **1a** disappeared immediately. A quantitative yield of 1-nitro-2-phenylpent-4-ene **3a** was observed after workup of the reaction, and the crude mixture was checked by NMR and purified by flash-column chromatography (Scheme 2, and entry 1 of Table 1).^[11]

Entry	1	\mathbb{R}^1	R ²	R ³	AlCl ₃ (eq)	Time (min)	3	Yield (%)
1	1a	Ph	Н	Н	_	2	3a	100
2	1a	Ph	Н	Н	_	2	3a	38 ^{<i>a</i>}
3	1b	4-MeOC ₆ H ₄	Н	Н	_	2	3b	100
4	1c	2-MeOC ₆ H ₄	Н	Н	-	2	3c	100
5	1d	$4-CIC_6H_4$	Н	Н	-	2	3d	94
6	1e	2-thienyl	Н	Н	-	2	3e	100
7	1f	Ph	Me	Н	_	5	3f	41
8	1g	Ph	Ph	Н	_	5	3g	26
9	1h	Bu	Н	Н	_	2	3h	65
10	1h	Bu	Н	Н	1	2	3h	70
11	1h	Bu	Н	Н	3	2	3i	81
12	1i	$R^1 + R^3 = -($	$CH_{2})_{4} - $	$R^2 = H$	_	2	3i	61 ^b
13	1i	$R^1 + R^3 = -($	$CH_{2})_{4} - $	$R^2 = H$	3	2	3i	70^{b}
14	1j	Et	Et	Н	_	5	3j	55 ^c
15	1j	Et	Et	Н	3	5	3j	81 ^d

Table 1. Reaction of nitroalkene 1 and triallylaluminum 2 to generate 4,5-unsaturated nitroalkenes 3

^aTwo equivalents of benzoyl peroxide were added to the solution before **2** was added.

^bTwo diastereomers were observed in the crude 1H-NMR but inseparable after the flash column purification.

^c37% of nitroalkene **3j** and 18% of nitrone **4j** were isolated.

^d43% of **3j** and 38% of **4j** were isolated.

3679

However, only 38% of **3a** but no 1-phenyl-1,4-pentadiene (PhCH=CH-CH₂-CH=CH₂) were isolated when 2 equiv of benzoyl peroxide, a freeradical initiator, were added to the solution (entry 2). This indicates that **1a** can only react with **2** via an ionic 1,4-conjugate addition because the presence of benzoyl peroxide had no effect on the reaction. The decrease in **3a** can be explained by the assumption that benzoyl peroxide also can react with or destroy the aluminum reagent. Similarly, high yields (94–100%) of **3b**-**e** were observed when β -nitrostyrenes **1b**-**e** were reacted with **2**, respectively (entries 3–6). All of these results are consistent with the literature reports that aryl substituted β -nitrostyrenes react with allylic metals to generate high yields of the conjugate addition products.^[2]

The reactions are very sensitive to steric effects. When the hindered nitroalkene 1-nitro-2-phenylpropene $1f^{[12a-c]}$ or 1,1-diphenyl-2-nitroethene $1 g^{[13]}$ was reacted with 2, only 41% of 3f or 26% of 3g (entries 7 and 8) were isolated, and the yields are much lower compared to the yields of 3a-e (entries 1–6). A possible explanation for this is that the substitution of the hydrogen atom by a methyl or phenyl group dramatically increases the steric hindrance between the nitroalkene and 2, thus retarding the conjugate addition to some degree.

Not only the mono- or di-aryl substituted β -nitrostyrenes **1a**-**g** but also the β -alkyl substituted 1-nitrohex-1-ene **1h** reacts with **2** as described previously. However, 3h was isolated in only 65% yield (entry 9), but the yield was increased to 70% when 1 equiv of aluminum chloride AlCl₃ was added (entry 10). Although the possibility of the formation other organoalumicompounds such (CH₂=CHCH₂)_xAlCl_yBr_{3-x-y} num as or $(CH_2 = CHCH_2)_x AlCl_v Br_{4-x-v}$ cannot be excluded after adding AlCl₃, the presence of AlCl₃ was found to improve and increase the product yields substantially. Surprising, the yield of **3h** increased to 81% when 3 equiv of AlCl₃ were added to the solution under similar conditions (entry 11). Similarly, a 61% yield of two inseparable diastereomers **3i** was also isolated when α,β disubstituted nitroalkenes such as 1-nitrocyclohexene 1i were reacted with 2 under similar conditions (entry 12), and the yield increased to 70% in the presence of 3 equiv of AlCl₃, as described previously (entry 13). Compared to β -nitrostyrenes **1a**-e, which always generate high yields of product, the use of β -alkyl substituted 1-nitrohex-1-ene **1h** leads to a lower yield of **3h** in the absence of AlCl₃ because polymers and/or intractable products may have been formed during reaction. A possible explanation for this is that triallylaluminum reagent 2 not only functions as a nucleophile but also as a Lewis acid to form a complex or coordinates with the aryl group and/or the oxygen atom of the nitro group of β -nitrostyrenes of 1a-e to stabilize the transition state or intermediate, thus retarding the formation of side reaction products, such as polymers. In the case of the α,β -disubstituted nitroalkene 1i, the generation of a slightly lower yield of 3i than 3h indicates that the presence of the disubstituted group at the α -position and β -position increases the steric hindrance, as described previously. However, the reactions of both 1h

and **1i** were improved by the addition the Lewis acid $AlCl_3$. Compared to the use of the allyl Grignard reagent to react with **1h** or **1i** to generate intractable reaction mixtures,^[2] the use of **2** leads to much better results in the presence of $AlCl_3$.

In addition to the nitroalkenes **1a**–**i**, other highly hindered nitroalkenes such as 2-ethyl-1-nitrobutene **1j**^[13a,b] were also studied. For example, 55% of the final products including 37% of the expected product nitroalkene **3j** and 18% of the unexpected product nitrone [Et₂C(CH₂CH=CH₂)-CHN(O)CH₂CH=CH₂] **4j** were isolated (entry 14). Surprisingly, the yield dramatically increased to 81%, including 43% of **3j** and 38% of **4j**, when 3 equiv of AlCl₃ were added (entry 15). Compared to the α -monosubstituted, β -monosubstituted, or α,β -disubstituted nitroalkenes that have been reported in the literature,^[2–7] substrate **1j** also reacted rapidly with **2** to generate moderate yields of product in both the absence or presence of AlCl₃, but the yield was higher in the presence of AlCl₃.

Based on these results, we conclude that 2 reacts with α,β -unsaturated nitroalkene 1 to undergo a 1,4-conjugate addition, similar to other allyl organometallic reagents. Compared to the allyl Grignard reagent^[2] or a tetraorganoalanate $R_3AlR'M$ (R' = allyl or phenyl) or $R_2AlR'_2MgX$ (R' = allyl, phenyl),^[6] the use of 2 has certain advantages. First, the use of an allyl Grignard reagent to react with 1h and 1i at -78° C gave an intractable reaction mixture whereas the use of 2 generated 65% or 81% of 3h and 61% or 70% of 3i at 0°C in the absence or presence of AlCl₃. Second, no product was generated and only the unreacted nitroalkene was recovered when triisobutylaluminum or diethylallylaluminum was reacted with 1i in diethyl ether, and the use of Et_2AlR_2MgX (R = allyl) requires 30 min to complete the reaction at room temperature, whereas the use of 2 requires only 2 min. Third, the preparation of the triallylalumium reagent 2 from aluminum metal and allyl bromide under reflux is a much simpler procedure compared to the formation of Et_2AlR_2MgX (R = allyl) from Et₂AlCl and RMgCl (R = allyl) at 0° C and then at -15° C. Fourth, **2** is a triorganoalane, and Et₂AlR₂MgX is a tetraorganoalanate, but 2 can also react with α,β -unsaturated nitro olefins to undergo exclusively conjugate addition, which is different from the allyl Grignard reagent, which can also undergo 1,2- and/ or 1,4-additions in some cases.

Finally, the proposed mechanism for the generation of nitroalkane 3a, which was obtained from the reaction of β -nitrostyrene 1a and triallylaluminium reagent 2 under a nitrogen atmosphere, is shown as Scheme 3. First, the 1,4-addition occurs to yield the intermediate nitronate I, and then I can obtain the proton from the dilute aqueous HBr solution to produce the final product.

Triallylaluminum reagent **2**, compared to other organometallic reagents, has some advantages: (1) short reaction time, (2) easy preparation, (3) operationally simple procedure, and (4) broadest substrate scope. For example, the allylzinc reagents always need longer reaction times (0.5-4.5 h) to complete the reaction.^[4] Similarly, the preparation of allylsamarium reagents needs



Scheme 3.

expensive samarium metal, and the reaction time is longer.^[3] The use of allyltin reagents in the presence of Lewis acid needs to undergo a 1.4-addition reaction. Even though mercuric chloride (about 0.4 mol%) was used in the preparation of triallylaluminum reagent, care has been taken to avoid the toxicity of allylmercury reagents.

CONCLUSION

3682

In summary, a simple, convenient, and efficient method for preparing the 4,5unsaturated nitroalkene **3** using α,β -unsaturated nitroalkene **1** and triallylalumium **2** in the absence or presence of AlCl₃ in ether under nitrogen at 0°C is described. The short reaction time and the simplicity of the procedures make this method one of the most efficient for the synthesis of this class of compounds. The most significant feature of this reaction concerns the preparation of triallylalumium, from allyl bromide and pure elemental Al,^[9,10] unlike previous procedures in which alkylaluminum and allylmagnesium chloride were used.^[11]

EXPERIMENTAL

General

All reactions were performed in oven-dried glassware under nitrogen. ¹H and ¹³C NMR spectra were recorded with a Bruker EX 400 FT NMR. ¹H NMR

chemical shifts are expressed in parts per million downfield from tetramethylsilane with reference to internal residual CHCl₃ (δ = 7.26 ppm) in CDCl₃. ¹³C NMR chemical shifts are expressed in parts per million downfield from CDCl₃ as an internal standard (δ = 77.0 ppm) in CDCl₃. GC-MS data were acquired using a HP 5890 GC/HP 5973 MSD mass spectrometer. Mass spectra were obtained on a Jeol JMS-D300 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Jeol JMS-HX 110 spectrometer.

Starting Materials

trans- β -Nitrostyrene **1a** and analogues **1b**-**h** were prepared according to literature procedures with minor modifications. 1-Nitro-cyclohexene **1j** was purchased from Aldrich Chemical Co. and was used without purification.

The Formation of Triallylaluminum $2^{[9,10]}$

A dry 250-mL flask fitted with a mechanical stirrer is assembled with a vacuum seal, a dropping funnel, and a reflux condenser to which a nitrogen inlet and an oil bubbler are attached. The flask is charged with aluminum granules (2.7 g, 0.1 mol), mercuric chloride (0.1 g), and iodine (0.1 g), and then the apparatus is thoroughly flushed with dry nitrogen. Ether (65 mL) and allyl bromide (freshly distilled, 10 mL) are added successively via the dropping funnel. The rest of allyl bromide (25 mL) is slowly added at rate sufficient to maintain a gentle reflux. The mixture is stirred for 5-6 h under refluxing conditions until the aluminum metal reacted completely.

Typical Experimental Procedures for the Preparation **3a** from the Reaction of β -Nitrostyrene **1a** and Triallylaluminum Reagent **2**

Triallylaluminun reagent 2 (0.85 mmol, 0.5 M × 1.7 mL) was added rapidly to a stirred solution of β -nitrostyrene **1a** (1 mmol) in ether (2 mL) at 0°C under nitrogen. The yellow color of **1a** disappeared immediately. After stirring for 2 min, the nitronates solution was added to an ice-cold and dilute hydrochloric acid solution at the same temperature. The solution was extracted with diethyl ether (25 mL × 3), and the ether solution was dried over MgSO₄, filtered, and evaporated to give an oily mixture. Quantitative yield of 1-nitro-2-phenylpent-4-ene **3a** was obtained after the crude mixture was checked by ¹H NMR, and the mixture was purified by flashcolumn chromatography using hexane–ethyl acetate as the eluent to obtain the pure products. All spectral data are consistent with the literature reports. Spectral data **3a**,^[3] **3b**,^[3] **3d**,^[3] **3e**^[4], and **3i**^[6b] are consistent with the literature. 1-Nitro-2-phenylpent-4-ene (**3a**)^[3]

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 7.20 Hz, 2H), 7.25 (tt, J = 7.20, 2.08 Hz, 1H), 7.32 (dd, J = 7.20, 2.08 Hz, 2H), 5.71–5.60 (m, 1H), 5.09–5.03 (m, 2H), 4.62 (dd, J = 12.10, 6.84 Hz, 1H), 4.54 (dd, J = 12.10, 8.44 Hz, 1H), 3.56 (quint, J = 7.36 Hz, 1H), 2.52–2.39 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 139.15, 134.12, 128.81, 127.56, 127.35, 118.09, 79.80, 43.69, 37.58. MS m/z (relative intensity) 191 (M⁺, tr), 143 (18), 129 (21), 104 (100), 91 (47).

1-Nitro-2-(4-methoxyphenyl)pent-4-ene (3b)^[3]

Colorless oil, ¹H NMR (400 MHz, CDCl₃): the pattern of the aromatic protons is AA'XX' and is simplified as δ 7.13 (dt, J = 8.72, 2.96 Hz, 2H), 6.88 (dt, J = 8.72, 2.96 Hz, 2H), and the other protons are 5.73–5.63 (m, 1H), 5.11–5.05 (m, 2H), 4.61 (dd, J = 12.10, 6.76 Hz, 1H), 4.51 (dd, J = 12.10, 8.60 Hz, 1H), 3.79 (s, 3H), 3.53 (quint, J = 7.36 Hz, 1H), 2.49–2.40 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.83, 134.29, 131.01, 128.34, 117.90, 114.14, 80.06, 55.07, 42.98, 37.60. MS m/z (relative intensity) 221 (M⁺, 8), 180 (11), 134 (100), 121 (14), 91 (15).

1-Nitro-2-(2-methoxyphenyl)pent-4-ene (3c)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.26 (td, J = 8.04, 1.60 Hz, 1H), 7.12 (dd, J = 7.48, 1.60 Hz, 1H), 6.94 (dd, J = 7.48, 1.60 Hz, 1H), 6.90 (td, J = 8.04, 1.60 Hz, 1H), 5.74–5.64 (m, 1H), 5.10-5.02 (m, 2H), 4.69 (dd, J = 12.30, 7.52 Hz, 1H), 4.63 (dd, J = 12.30, 7.04 Hz, 1H), 3.87 (quint, J = 7.32 Hz, 1H), 3.86 (s, 3H), 2.62–2.47 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 157.27, 134.96, 128.76, 128.59, 127.03, 120.71, 117.54, 110.96, 78.46, 55.32, 39.15, 35.81. MS m/z (relative intensity) 221 (M⁺, 20), 180 (22), 134 (100), 119 (55), 91 (54). HRMS calcd. for C₁₂H₁₅NO₃ (M⁺) 221.1052, found 221.1054.

1-Nitro-2-(4-chlorophenyl)pent-4-ene (3d)^[3]

Colorless oil, ¹H NMR (400 MHz, CDCl₃): the pattern of the aromatic protons is AA'XX' and is simplified as δ 7.29 (dt, J = 8.48, 2.64 Hz, 2H), 7.11 (dt, J = 8.48, 2.64 Hz, 2H), and the other protons are 5.67–5.55 (m, 1H), 5.07–5.03 (m, 2H), 4.61 (dd, J = 12.60, 6.48 Hz, 1H), 4.52 (dd, J = 12.60, 8.92 Hz, 1H), 3.54 (quint, J = 7.24 Hz, 1H), 2.44–2.39 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 137.66, 133.72, 133.34, 128.98, 128.75, 118.44, 79.54, 43.10, 37.46. MS m/z (relative intensity) 225 (M⁺, tr), 178 (18), 141 (35), 138 (100), 125 (30), 103 (20).

2-(1-Nitropent-4-en-2-yl)thiophene (3e)^[4]

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, J = 5.12, 1.08 Hz, 1H), 6.94 (dd, J = 5.12, 3.44 Hz, 1H), 6.87 (dd, J = 3.44, 1.08 Hz, 1H), 5.78–5.67 (m, 1H), 5.17–5.10 (m, 2H), 4.63 (dd, J = 12.50, 6.68 Hz, 1H), 4.53 (dd, J = 12.50, 8.16 Hz, 1H), 3.91 (quint, J = 7.44 Hz, 1H), 2.58–2.44 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 142.14, 133.65, 126.95, 125.26, 124.51, 118.72, 80.19, 39.13, 38.50. MS m/z (relative intensity) 197 (M⁺, tr), 150 (25), 110 (100), 97 (23).

1-Nitro-2-methyl-2-phenylpent-4-ene (3f)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.34 (m, 4H), 7.28 (tt, J = 7.00, 1.60 Hz, 1H), 5.59–5.48 (m, 1H), 5.14–5.08 (m, 2H), 4.63 (d, J = 11.12 Hz, 1H), 4.59 (d, J = 11.12 Hz, 1H), 2.71 (dd, J = 13.92, 6.40 Hz, 1H), 2.51 (dd, J = 13.92, 8.04 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.17, 132.75, 128.69, 127.17, 126.11, 119.41, 85.28, 44.21, 42.11, 22.75. MS m/z (relative intensity) 205 (M⁺, tr), 164 (21), 118 (92), 117 (100), 91 (32). HRMS calcd. for C₁₂H₁₅ [(M-NO₂)⁺] 159.1174, found 159.1164.

1-Nitro-2,2-diphenylpent-4-ene (3g)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 7.33 (tt, *J* = 8.32, 1.80 Hz, 4H), 7.27 (tt, *J* = 7.20, 2.08 Hz, 2H), 7.12 (dt, *J* = 7.20, 1.80 Hz, 4H), 5.16 (s, 2H), 5.19–5.10 (m, 1H), 3.19 (d, *J* = 6.24 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.50, 132.75, 128.39, 127.48, 127.11, 120.43, 81.75, 50.25, 41.10. MS *m*/*z* (relative intensity) 267 (M⁺, tr), 226 (61), 180 (100), 165 (43). HRMS calcd. for C₁₇H₁₇NO₂ (M⁺) 267.1259, found 267.1265.

1-Allyl-2-nitrohexane (3h)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 5.86–5.66 (m, 1H), 5.13-5.09 (m, 2H), 4.34 (dd, J = 12.00, 6.80 Hz, 1H), 4.28 (dd, J = 12.00, 8.40 Hz, 1H), 2.35–2.07 (m, 3H), 1.45–1.20 (m, 6H), 0.94 (t, J = 6.76 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 134.36, 118.24, 79.01, 37.05, 35.52, 30.74, 28.44, 22.62, 13.89. MS m/z (relative intensity) 171 (M⁺, tr), 110 (31), 81 (75), 67(82), 55(100), 41(90). HRMS calcd. for C₉H₁₇ [(M-NO₂)⁺] 125.1330, found 125.1329.

1-Allyl-2-nitrocyclohexane (3i)^[6b]

Colorless oil; two isomers were observed by NMR after workup of the reaction, and these two isomers were inseparable even after the mixture was purified by column chromatography and then by HPLC. The ¹H NMR

spectral data of the mixture of these two isomers are ¹H NMR (400 MHz, CDCl₃) δ 5.77–5.66 (m, 1H), 5.12–5.01 (m, 2H), 4.63 (quint, J = 3.84 Hz, 0.84H), 4.25 (td, J = 11.20, 4.04 Hz, 0.16H), 2.32–0.80 (m, 11H). ¹³C NMR (100 MHz, CDCl₃) δ 135.37, 134.16, 117.80, 117.22, 90.41, 85.84, 40.26, 38.66, 36.92, 33.78, 31.94, 29.42, 27.51, 26.66, 24.69, 24.37, 22.18, 21.93. MS m/z (relative intensity) 169 (M⁺, tr), 107 (26), 93 (36), 81 (100), 79 (56), 67 (55), 41 (43).

1-Nitro-2,2-diethylpent-4-ene (3j)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 5.85–5.75 (m, 1H), 5.19–5.15 (m, 2H), 4.28 (s, 2H), 2.12 (d, J = 7.60 Hz, 2H), 1.36 (q, J = 7.40 Hz, 4H), 0.91 (t, J = 7.40 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 132.62, 119.33, 80.11, 41.11, 38.04, 26.30, 7.22. MS m/z (relative intensity) 171 (M⁺, tr), 110 (53), 95 (41), 83 (73), 55 (100), 41 (46). HRMS calcd. for C₉H₁₇ [(M-NO₂)⁺] 125.1330, found 125.1329.

C-(3-Ethyl-hex-1-ene)-N-allylnitrone (4j)

Colorless oil, ¹H NMR (400 MHz, CDCl₃) δ 6.35 (s, 1H), 6.12–6.02 (m, 1H), 5.75–5.65 (m, 1H), 5.43-5.37 (m, 2H), 5.11–5.02 (m, 2H), 4.37 (d, J = 6.64 Hz, 2H), 2.50 (d, J = 7.48 Hz, 2H), 1.83–1.67 (m, 4H), 0.81 (t, J = 7.60 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 143.25, 134.46, 130.73, 121.31, 117.45, 69.51, 43.33, 36.60, 25.41, 8.28. MS m/z (relative intensity) 195 (M⁺, tr), 105 (16), 91 (100), 77 (12), 69 (13), 55 (15). HRMS calcd. for C₁₂H₂₁NO (M⁺) 195.1623, found 195.1622.

ACKNOWLEDGMENTS

Financial support by National Taiwan Normal University ORD 93-C and National Science Council of the Republic of China is gratefully acknowledged. We also thank Professor Milton S. Feather for helpful discussions during the preparation of the manuscript.

REFERENCES

 (a) Corey, E. J.; Estreicher, H. J. Am. Chem. Soc. 1978, 100, 6294; (b) Seebach, D.; Colvin, E. W.; Weller, T. Chimia 1979, 33, 1; (c) Barrett, A. G. M.; Graboski, G. G. Chem. Rev. 1986, 86, 751; (d) Rosini, G.; Ballini, R. Synthesis 1988, 833; (e) Nitroalkanes and Nitroalkenes in Synthesis Tetrahedron 1990, 46, 7313; (f) Barrett, A. G. M. Chem. Soc. Rev. 1991, 20, 95; (g) Ono, N. The Nitro Group in Organic Synthesis; Wiley-vch: New York, 2001; (h) Padwa, A.; Pearson, W. H. Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products; John Wiley & Sons: NJ, 2003.

- Barboni, L.; Bartoli, G.; Marcantoni, E.; Petrini, M.; Dalpozzo, R. J. Chem. Soc., Perkin Trans. 1 1990, 2133.
- 3. Bao, W.; Zheng, Y.; Zhang, Y. J. Chem. Res., Synop. 1999, 732.
- Kumar, H. M. S.; Reddy, B. V. S.; Reddy, P. T.; Yadav, J. B. *Tetrahedron Lett.* 1999, 40, 5387.
- 5. (a) Ochiai, M.; Arimoto, J.; Jujita, E. *Tetrahedron Lett.* 1981, 22, 1115;
 (b) Uno, H.; Fujiki, S.; Suzuki, S. Bull. Chem. Soc. Jpn. 1986, 59, 1267;
 (c) Yamamoto, Y.; Nishii, S. J. Org. Chem. 1988, 53, 3597.
- (a) Pecunioso, A.; Menicagli, R. J. Org. Chem. 1988, 53, 45; (b) Pecunioso, A.; Menicagli, R. J. Org. Chem. 1989, 54, 2391; (c) Menicagli, R.; Malanga, C.; Guagnano, V. Tetrahedron Lett. 1992, 33, 2867.
- 7. (a) Yao, C.-F.; Chen, W.-C.; Lin, Y.-M. *Tetrahedron Lett.* **1996**, *37*, 6339;
 (b) Yao, C.-F.; Kao, K.-S.; Liu, J.-T.; Chu, C.-M.; Wang, Y.; Chen, W.-C.; Lin, Y.-M.; Yan, M.-C.; Liu, J.-Y.; Chuang, C.-M.; Shiue, J.-L. *Tetrahedron* **1998**, *54*, 791; (c) Chu, C.-M.; Liu, J.-T.; Lin, W.-W.; Yao, C.-F. J. Chem. Soc., Perkin Trans. 1 **1999**, *47*.
- 8. Shen, K.-H.; Yao, C.-F. J. Org. Chem. 2006, 71, 3980.
- Triallylaluminum 2 was prepared according to the procedures in the following; Komiya, S. Synthesis of Organometallic Compounds; John Wiley & Sons: New York, 1997.
- The concentration of triallylaluminum 2 was determined by the following methods; (a) Gilman, H.; Haubein, A. H. J. Am. Chem. Soc. 1944, 66, 1515; (b) Bergbreiter, D. E.; Pendergrass, E. J. Org. Chem. 1981, 46, 219; (c) Bowen, M. E.; Aavula, B. R.; Mash, E. A. J. Org. Chem. 2002, 67, 9087.
- (a) Paley, R. S.; Snow, S. R. *Tetrahedron Lett.* **1990**, *31*, 5853; (b) Rainier, J. D.; Cox, J. M. Org. Lett. **2000**, *2*, 2707; (c) Allwein, S. P.; Cox, J. M.; Howard, B. E.; Johnson, H. W. B.; Rainier, J. D. *Tetrahedron* **2002**, *58*, 1997.
- (a) Lin, W.-W.; Jang, Y.-J.; Wang, Y.; Liu, J.-T.; Hu, S.-R.; Wang, L.-Y.; Yao, C.-F. J. Org. Chem. 2001, 66, 1984; (b) Jang, Y.-J.; Lin, W.-W.; Shih, Y.-K.; Liu, J.-T.; Hwang, M.-H.; Yao, C.-F. Tetrahedron 2003, 59, 4979; (c) Ohta, H.; Kobayashi, N.; Ozaki, K. J. Org. Chem. 1989, 54, 1802.
- 13. Bordwell, F. G.; Garbish, E. W. J. J. Org. Chem. 1962, 27, 3049.