

Free radical reactions to generate alkenes and/or ionic reactions to generate hydroximoyl chlorides when β -nitrostyrenes react with triethylaluminium or diethylaluminium chloride

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β -Nitrostyrenes **1** react with triethylaluminium or diethylaluminium chloride in diethyl ether solution and under nitrogen or argon to generate the alkenes **2** and the hydroximoyl chlorides **3** after work-up with ice-cold, conc. hydrochloric acid. The formation of the alkenes **2** is proposed to be a free-radical reaction *via* NO_2 /alkyl substitution since the yields of the alkenes **2** are increased in the presence of benzoyl peroxide (Bz_2O_2) and decreased in the presence of galvinoxyl. Only the alkenes **2** are produced with a high stereoselectivity for the *E* isomers when β -nitrostyrenes react with triethylaluminium in the presence of one to two equivalents of Bz_2O_2 as free-radical initiator. The mechanism of the generation of the hydroximoyl chlorides **3** is proposed to proceed through a 1,4-addition pathway to produce nitronates **A**, then the protonated nitronates **B** or the nitroso cations **C** are trapped by chloride ion to form the final products. The yields of compounds **3** are also improved by the presence of Lewis acids such as MgCl_2 . Medium to high yields of the hydroximoyl chlorides **3** and traces or low yields of the alkenes **2** are generated when triethylaluminium or diethylaluminium chloride react with β -nitrostyrenes in the presence of three equivalents of MgCl_2 under argon.

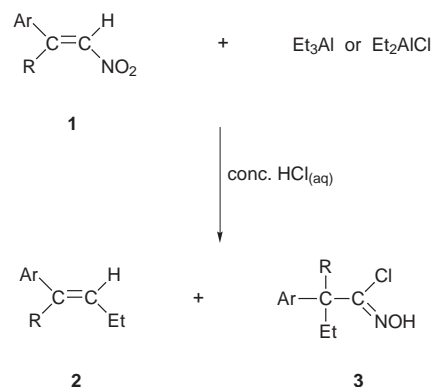
Introduction

Reactions of non-stabilized organometallic reagents, such as the alkyl derivatives of lithium,¹ magnesium,² zinc,³ and copper,⁴ with conjugated nitroalkenes to generate nitroalkanes or carbonyl compounds have been studied in recent years. Reactions of trialkylaluminium and triorganoaluminium-ether complexes with α,β -unsaturated nitroalkenes to give 1,4-alkylated products in high yield have been reported.⁵ It is also reported that β -nitrostyrenes can react with dialkylzinc,⁶ organomanganese,⁷ *t*-BuHgX/KI,⁸ trialkylgallium⁹ or trialkylborane¹⁰ reagents, respectively, to generate alkenes and/or nitroalkanes and the mechanism is proposed to be an ionic or free-radical reaction. Barton has shown that the nitroolefins reacted with thiopyridone-based esters to generate α -nitro sulfides by free-radical chain reactions.¹¹ It was concluded that nitroalkenes are highly reactive conjugate acceptors and useful intermediates in organic synthesis and can react with non-stabilized nucleophiles to generate different products under different work-up conditions.¹⁻¹¹

In 1989 Kunz observed that dialkylaluminium chlorides react with α,β -unsaturated carboxylic acid derivatives to give 1,4-addition products.¹² This interesting study indicates that dialkylaluminium chlorides also can be used as nucleophiles in the Michael reaction. In this paper, we report the reactions of β -nitrostyrenes **1** with triethylaluminium or diethylaluminium chloride to generate free-radical and/or ionic products depending upon the reaction conditions.

Results and discussion

Reactions of β -nitrostyrenes **1** with triethylaluminium or diethylaluminium chloride in diethyl ether solution at 40 or 60 °C (oil-bath temperature) and under nitrogen or argon gave two products after the reaction intermediates were slowly added to ice-cold, conc. hydrochloric acid. One of the products was assigned to be the 1-arylbut-1-ene **2** and the other was the



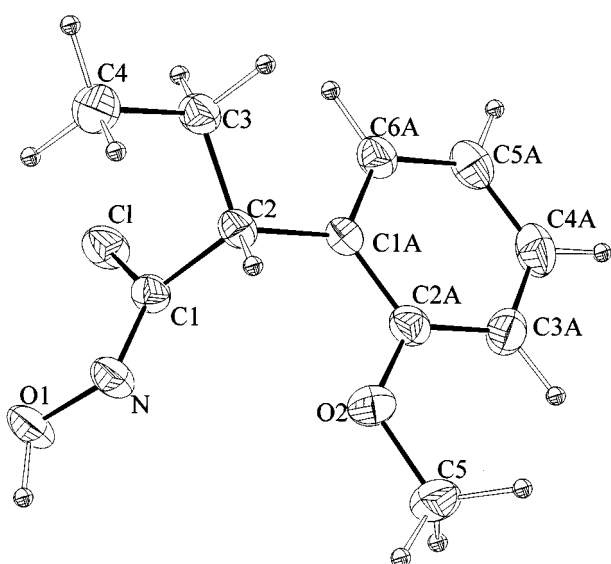
- a: Ar = Ph, R = H
- b: Ar = 4-MeC₆H₄, R = H
- c: Ar = 4-MeOC₆H₄, R = H
- d: Ar = 4-FC₆H₄, R = H
- e: Ar = 4-CF₃C₆H₄, R = H
- f: Ar = 2-MeOC₆H₄, R = H
- g: Ar = 2-MeC₆H₄, R = H
- h: Ar = 2-CF₃C₆H₄, R = H
- i: Ar = 2-thienyl, R = H
- j: Ar = 2-furyl, R = H
- k: Ar = Ph, R = Ph
- l: Ar = Ph, R = Me

hydroximoyl chloride **3** according to their ¹H, ¹³C NMR, IR, and mass spectra after flash column chromatographic purification (Table 1).

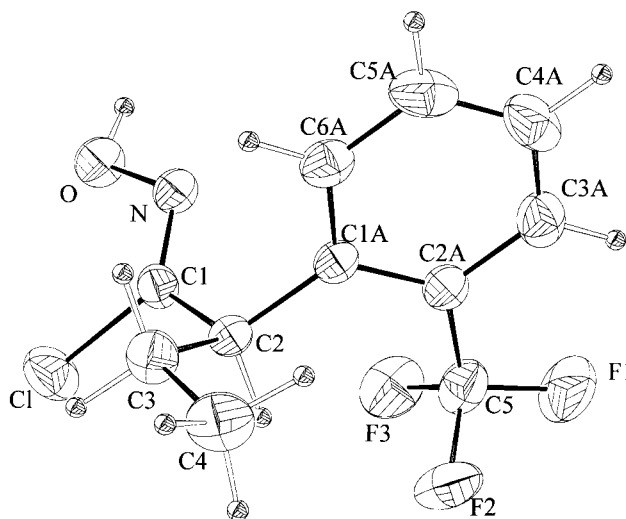
Table 1 Reactions of β -nitrostyrenes **1** with Et_3Al or Et_2AlCl under nitrogen or argon

Entry	Substrate	Et_3Al or Et_2AlCl	Conditions ^a	2 (%) ^b	3 (%) ^b	2 : 3
1	1a	Et_3Al	N_2 , 60 °C, 4 h	2a (24)	3a (49)	33:67
2	1a	Et_2AlCl	N_2 , 60 °C, 7 h	2a (22)	3a (36) ^c	38:62
3	1b	Et_3Al	N_2 , 60 °C, 2 h	2b (30)	3b (35)	46:54
4	1b	Et_3Al	Ar, 60 °C, 3 h	2b (25)	3b (57) ^a	30:70
5	1b	Et_3AlCl	N_2 , dark, rt, 9 h	2b (18)	3b (41) ^e	31:69
6	1b	Et_2AlCl	N_2 , 60 °C, 2 h	2b (19)	3b (33) ^f	37:63
7	1b	Et_2AlCl	N_2 , 60 °C, 9 h	2b (38)	3b (51) ^g	43:57
8	1b	Et_2AlCl	Ar, 60 °C, 9 h	2b (28)	3b (44) ^h	39:61
9	1c	Et_3Al	N_2 , 40 °C, 3 h	2c (19)	3c (38)	33:67
10	1d	Et_3Al	N_2 , rt, 18 h	2d (24)	3d (32)	43:57
11	1e	Et_3Al	N_2 , 40 °C, 2 h	2e (25)	3e (40)	38:62
12	1e	Et_2AlCl	N_2 , 40 °C, 6 h	2e (24)	3e (32)	43:57
13	1f	Et_3Al	N_2 , 40 °C, 6 h	2f (29)	3f (31)	48:52
14	1g	Et_3Al	N_2 , 40 °C, 5.5 h	2g (43)	3g (29)	60:40
15	1g	Et_2AlCl	N_2 , 40 °C, 6 h	2g (32)	3g (55)	37:63
16	1h	Et_3Al	N_2 , 40 °C, 5 h	2h (39)	3h (28)	58:42
17	1i	Et_3Al	N_2 , 40 °C, 5 h	2i (18)	3i (27)	40:60
18	1i	Et_2AlCl	N_2 , 40 °C, 6 h	2i (tr)	3i (51)	<1:99
19	1j	Et_3Al	N_2 , rt, 5 h	2j (22)	3j (27)	45:55
20	1k	Et_3Al	N_2 , 40 °C, 4 h	2k (29)	3k (58)	33:67
21	1k	Et_2AlCl	N_2 , 40 °C, 6 h	2k (35)	3i (43)	45:55
22	1l	Et_3Al	N_2 , 40 °C, 8 h	2l (14)	3l (58) ⁱ	19:81

^a Oil-bath temperature. ^b Isolated yields, tr = trace. ^c 11% Unchanged compound **1a** was recovered. ^d 15% Unchanged compound **1b** was recovered. ^e 40% Unchanged compound **1b** was recovered. ^f 48% Unchanged compound **1b** was recovered. ^g 10% Unchanged compound **1b** was recovered. ^h 17% Unchanged compound **1b** was recovered. ⁱ 9% Unchanged compound **1l** was recovered.

**Fig. 1** Molecular structure of compound **3f**.

The formation of the different products indicates that triethylaluminium and diethylaluminium chloride can generate the alkenes **2** and the hydroximoyl chlorides **3** simultaneously under similar experimental and work-up conditions. It is also found that triethylaluminium is always more reactive than diethylaluminium chloride when substrates **1a** (entries 1 and 2), **1b** (entries 3 and 6 or entries 4 and 8), **1e** (entries 11 and 12), and **1k** (entries 20 and 21), respectively, reacted with triethylaluminium or diethylaluminium chloride under the same conditions. Usually conjugate addition was predominant with the yields of the hydroximoyl chlorides **3** higher than the alkenes **2** when β -nitrostyrenes **1** reacted with triethylaluminium or diethylaluminium chloride. However, with the *ortho* substituted β -nitrostyrenes **1f** (entry 13), **1g** (entry 14), or **1h** (entry 16), the results were reversed and the yields of the alkenes **2** were almost equal to or even higher than those of hydroximoyl chlorides **3** when triethylaluminium was used. These different results can be attributed to the steric effect of the OCH_3 , CH_3 , and CF_3 groups at the *ortho* position of the benzene ring. The stereo-

**Fig. 2** Molecular structure of compound **3h**.

chemistry of compounds **3f** and **3h** has been determined by X-ray crystallography. Structures are shown in Fig. 1 (**3f**) and Fig. 2 (**3h**) and crystal data are listed in Table 2.^{†13}

Our previous work on the Michael addition of Grignard or organolithium reagents to β -nitrostyrenes showed that high yields of the hydroximoyl halides, nitrile oxides, or carboxylic acids were formed when the nitronates were treated with ice-cold, conc. hydrohalic or sulfuric acid solutions.¹⁴ A blue or green color always appeared when the nitronates were added to the acids. A similar blue-green color was observed again when the intermediates, aluminium nitronates **A**, were slowly added to ice-cold, conc. hydrochloric acid. The blue-green color indicated that the hydroximoyl chlorides **3** were formed from the

[†] Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/277. See <http://www.rsc.org/suppdata/perkin1/1999/47/> for crystallographic files in .cif format.

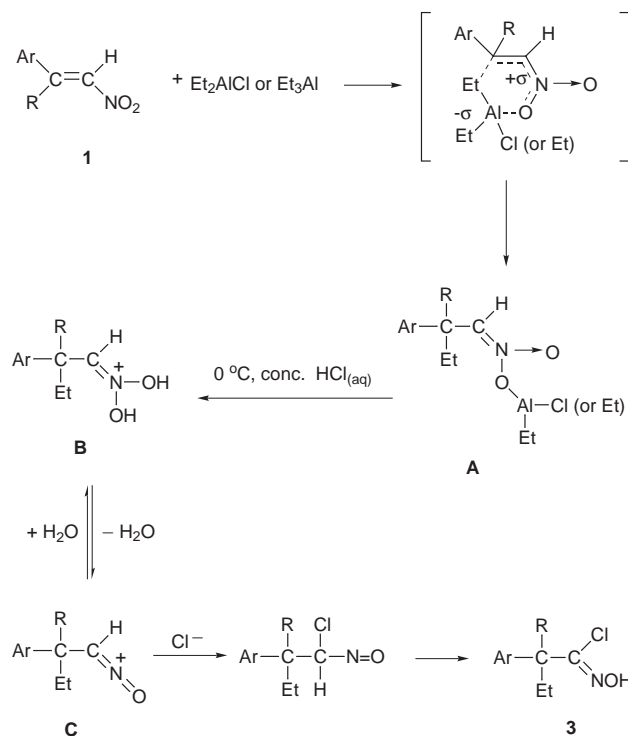
protonated nitronates **B** or the nitroso cations **C**, then intermediates **B** or **C** were trapped by chloride ion to yield a nitroso compound and this rearranged to give the final products (Scheme 1).

Lewis acids play an important role in the ionic reactions leading to hydroximoyl chlorides **3**. Thus, when three equivalents of MgCl_2 were added to the solution, the yields of products **3** were improved substantially when triethylaluminium or diethylaluminium chloride was also used under nitrogen or argon (Table 3). It appeared that MgCl_2 coordinated with the oxygen of the nitro group, as did the aluminium center of the organoaluminium reagents, to promote the ionic transfer of the ethyl group to the β -nitrostyrenes. Similar results are also observed when diethylzinc reacts with β -nitrostyrenes in Et_2O and in the presence of $\text{MgBr}_2/\text{MgCl}_2$ or copper salts¹⁵ as catalyst. We were also surprised to find that substrates **1c**, **1f**, **1i**, **1j**, and **1l** reacted with diethylaluminium chloride or triethylaluminium to generate medium to high yields (57–95%) of the hydroximoyl

Table 2 Crystallographic and refinement data for compounds **3f** and **3h**

	3f	3h
Empirical formula	$\text{C}_{11}\text{H}_{14}\text{ClNO}_2$	$\text{C}_{11}\text{H}_{11}\text{ClF}_3\text{NO}$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/a$	$Pcab$
Cell dimensions		
$a/\text{\AA}$	9.133(3)	7.870(3)
$b/\text{\AA}$	13.3169(19)	12.720(4)
$c/\text{\AA}$	9.4793(11)	23.955(7)
β ($^\circ$)	94.343(16)	
$V/\text{\AA}^3$	1149.5(5)	2397.9(13)
Crystal size/mm	$0.17 \times 0.27 \times 0.33$	$0.51 \times 0.45 \times 0.46$
Formula weight	227.69	265.66
Z	4	8
$F(000)$	455.94	1079.86
$D_c/\text{g cm}^{-3}$	1.316	1.472
μ/mm^{-1}	0.31	0.34
$\lambda/\text{\AA}$	0.70930	0.70930
2θ (max)	49.8	49.8
Diffractometer	Nonius (CAD-4)	Nonius (CAD-4)
Scan mode	θ/θ	θ/θ
hkl mode	$-10 < h < 10$,	$0 < h < 9$,
No. unique reflections	$0 < k < 15$,	$0 < k < 15$,
	$0 < l < 11$	$0 < l < 28$
	2020	2107
No. obsd $I_o > 2.5\sigma(I_o)$	1358	1489
Transmission factors	0.96–1.00	0.94–1.00
Parameters	137	155
R^*	0.039	0.046
R_w^*	0.028	0.036
Goodness of fit*	2.63	4.13
Maximum Δ/σ	0.016	0.004
D-map maximum/ $e \text{\AA}^{-3}$	0.200	0.220
D-map minimum/ $e \text{\AA}^{-3}$	-0.210	-0.320

* $R = \sum |F_o - F_c| / \sum F_o$, $R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$, $\text{GOF} = [\sum w(F_o - F_c)^2 / (N_{\text{obsd}} - N_{\text{param}})]^{1/2}$.



Scheme 1

chlorides **3**, while only a trace or none of the alkenes **2** (entries 3, 6, 9, 10, and 12) was observed. These results indicate that the methoxy, thienyl, and furyl groups also can coordinate with the aluminium reagents to promote the transfer of the ethyl group to the β -nitrostyrenes and the presence of the methyl group will increase the steric hindrance to retard the free-radical reaction.

Hydroximoyl halides are important intermediates in organic synthesis. Compared with the method of dehydration of primary nitro compounds (Mukaiyama–Hoshino),¹⁶ oxidation of aldoximes¹⁷ or the reaction of TiCl_4 with nitroalkenes¹⁸ to generate nitrile oxides or hydroximoyl chlorides, we found that alkylation and chlorination also could occur in a one-pot reaction to give medium to high yields of the hydroximoyl chlorides **3** from reactions of conjugated nitroalkenes with organoaluminium reagents.

The mechanism of the formation of alkenes **2** is proposed to be a free-radical non-chain reaction. The free-radical reaction is obviously stimulated by photolysis or by dibenzoyl peroxide (Table 4).^{19,20} Only 37–63% yields of the alkenes **2** were generated when solutions of β -nitrostyrenes **1** and triethylaluminium were irradiated with a 275 W General Electric sunlamp at $\sim 30^\circ\text{C}$. It is known that an $\text{S}_{\text{H}}2$ reaction can occur readily at an aluminium center.^{20,21} The yields of the alkenes **2** were also increased dramatically (35–80%) when one or two equivalents of benzoyl peroxide were added to the system at rt and in the

Table 3 Reactions of β -nitrostyrenes with Et_3Al or Et_2AlCl in the presence of 3 equivalents of MgCl_2 under nitrogen or argon

Entry	Substrate	Et_3Al or Et_2AlCl	Conditions	2 (%)	3 (%)	2:3
1	1a	Et_3Al	Ar, 60°C , 2.5 h	2a (17)	3a (83)	17:83
2	1b	Et_3Al	N_2 , 60°C , 3 h	2b (12)	3b (72)	14:86
3	1c	Et_2AlCl	Ar, 60°C , 4 h	2c (tr)	3c (95)	<1:99
4	1d	Et_2AlCl	Ar, 40°C , 17 h	2d (26)	3d (67)	28:72
5	1e	Et_2AlCl	Ar, 40°C , 10 h	2e (22)	3e (77)	22:78
6	1f	Et_2AlCl	Ar, 50°C , 6 h	2f (tr)	3f (78)	<1:99
7	1g	Et_2AlCl	Ar, 60°C , 11 h	2g (26)	3g (69)	27:73
8	1h	Et_2AlCl	Ar, 40°C , 12 h	2h (35)	3h (60)	37:63
9	1i	Et_2AlCl	Ar, 40°C , 2 h	2i (tr)	3i (57)	<1:99
10	1j	Et_2AlCl	Ar, rt, 8 h	2j (tr)	3j (62)	<1:99
11	1k	Et_3Al	N_2 , 40°C , 5 h	2k (33)	3k (60)	36:64
12	1l	Et_3Al	N_2 , 50°C , 3 h	2l (tr)	3l (70)	<1:99

Table 4 Reactions of β -nitrostyrenes with Et_3Al under nitrogen

Entry	Substrate	Conditions	2 (%)	3 (%)	2:3
1	1a	Bz_2O_2 , 10 mol%, rt, 13 h	2a (56)	3a	>99:1
2	1a	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2a (50)	3a	>99:1
3	1a	Bz_2O_2 , 2 equiv., rt, 13 h	2a (61)	3a	>99:1
4	1b	Bz_2O_2 , 2 equiv., rt, 5.5 h	2b (70)	3b	>99:1
5	1b	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2b (55)	3b	>99:1
6	1b	galvinoxyl 50 mol%, <i>hv</i> , 4 h	2b (17)	3b (tr)	>99:1
7	1c	Bz_2O_2 , 2 equiv., rt, 4.5 h	2c (35)	3c	>99:1
8	1d	Bz_2O_2 , 2 equiv., rt, 4 h	2d (72)	3d	>99:1
9	1d	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2d (61)	3d	>99:1
10	1e	Bz_2O_2 , 1 equiv., rt, 5 h	2e (68)	3e	>99:1
11	1e	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2e (59)	3e	>99:1
12	1f	Bz_2O_2 , 1 equiv., rt, 4.5 h	2f (52)	3f	>99:1
13	1f	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2f (54)	3f	>99:1
14	1g	Bz_2O_2 , 1 equiv., rt, 8 h	2g (72)	3g	>99:1
15	1g	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2g (60)	3g	>99:1
16	1h	Bz_2O_2 , 1 equiv., rt, 5 h	2h (62)	3h	>99:1
17	1h	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2h (63)	3h	>99:1
18	1i	Bz_2O_2 , 1 equiv., rt, 4 h	2i (65)	3i	>99:1
19	1i	Bz_2O_2 , 1 equiv., <i>hv</i> , 1.5 h	2i (54)	3i	>99:1
20	1j	Bz_2O_2 , 1 equiv., rt, 5 h	2j (43)	3j	>99:1
21	1j	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2j (37)	3j	>99:1
22	1k	Bz_2O_2 , 1 equiv., rt, 4 h	2k (80)	3k (14)	85:15
23	1k	Bz_2O_2 , 1 equiv., <i>hv</i> , 1.5 h	2k (62)	3k	>99:1
24	1l	Bz_2O_2 , 1 equiv., rt, 4 h	2l (40)	3l	>99:1
25	1l	Bz_2O_2 , 1 equiv., <i>hv</i> , 2 h	2l (38)	3l	>99:1

absence of irradiation. After observation of the positive effect of benzoyl peroxide, we also added 50 mol% of galvinoxyl, an efficient scavenger for free radicals,²² to the reaction system. With substrate **1b** unchanged starting material was recovered (74%) and only a 17% yield of compound **2b** was formed after the solution was irradiated with a sunlamp for 4 h (entry 6). It is also reported that only *E* products can be formed no matter which (*E*)- or (*Z*)- β -nitrostyrenes are used.⁶ Based on literature reports^{6–10} and our results (Tables 1–3), we can conclude that the substitution of the nitro group by the ethyl group apparently involves the radical addition/elimination with little evidence of a chain process. This proposed mechanism in Scheme 2 is totally different from Hassner's proposed mechanism.⁷ One

route to generate a variety of arylated (*E*)-alkenes in the presence of the radical initiator.

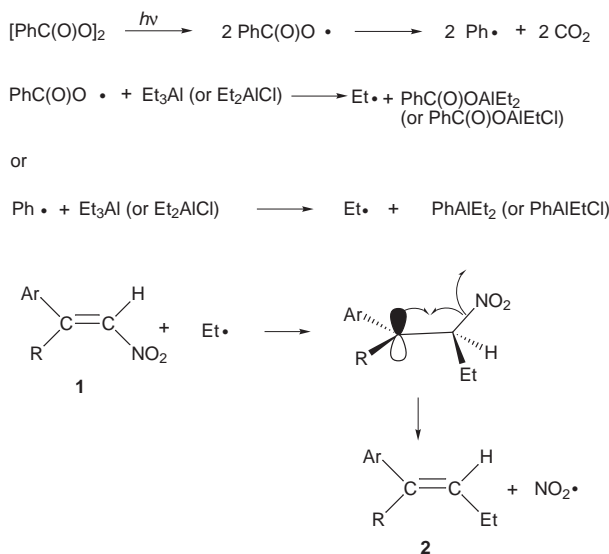
Experimental

General

All reactions were performed in flame- or oven-dried glassware under a positive pressure of nitrogen or argon. Air- and moisture-sensitive compounds were introduced by the use of a syringe or cannula through a rubber septum. Compounds **1a–e**, **1h–j**, diethylaluminium chloride, triethylaluminium and conc. hydrochloric acid (37%) were purchased from Aldrich. Compounds **1f,g**,²⁴ **1k**,²⁵ and **1l**²⁶ were prepared according to or by modifying the literature procedures. Diethyl ether was distilled from sodium–benzophenone ketyl and was degassed prior to reactions. Analytical TLC was performed with E. Merck silica gel 60F254 glass plates, and flash chromatography by the use of E. Merck silica gel 60 (230–400 mesh). GCMS were recorded on an HP 5890 GC/HP 5970B MSD spectrometer, and MS or high-resolution MS (HRMS) were measured by a JEOL JMS-D300 or JEOL JMS-HX1 10 spectrometer. ¹H and ¹³C NMR spectra were recorded on a JEOL Ex-400 or a Varian Gemini-200 spectrometer. All NMR data were obtained in CDCl_3 solution and chemical shifts δ are given in ppm relative to SiMe_4 . *J*-Values are given in Hz. Elemental analyses were performed by a Perkin-Elmer 2400 instrument. IR spectra were recorded in the FT mode by a JASCO IR-7000 spectrometer. All mp were determined with a MEL-TEMP II apparatus and were uncorrected.

Typical procedure for the reaction of β -nitrostyrenes **1** with triethylaluminium or diethylaluminium chloride (see Table 1)

A solution of 5 mmol of Et_3Al in 30 ml of diethyl ether was prepared from the commercially available 1.0 M Et_3Al in hexane. To this solution was slowly added a 0.1 M solution of (*E*)- β -nitrostyrene **1a** in diethyl ether (2 mmol in 20 ml) and the stirred mixture was refluxed at 60 °C (oil-bath temperature) under nitrogen. After the starting material had disappeared (4 h), the solution was slowly added to 100 ml of ice-cold, conc. hydrochloric acid and stirred for 30 min before extraction with CH_2Cl_2 . The CH_2Cl_2 solution was washed with brine, dried over MgSO_4 , filtered, and evaporated to obtain an

**Scheme 2**

possibility is that the addition of the ethyl radical generates the benzylic radical which undergoes β -elimination to yield the final product **2**.^{8,10,23} The generation of the (*E*)-1-arylbut-1-ene **2** indicated that the addition of the ethyl radical to β -nitrostyrenes **1** is regioselective. All these results showed that triethylaluminium reagent provides a highly stereoselective

oily mixture. The crude NMR yields of the products **2a** (24%) and **3a** (49%) were measured by using toluene or dibromomethane as an internal standard and the results are shown in Table 1. Flash column chromatography was used to separate the products by use of hexane to obtain (*E*)-1-phenylbut-1-ene **2a** as the least polar product, then use of hexane–ethyl acetate (99:1) as eluent to obtain the other product, 2-phenylbutanohydroximoyl chloride **3a**. Similar procedures were enacted when diethylaluminium chloride reacted with (*E*)- β -nitrostyrene **1a** to obtain products **2a** (22%) and **3a** (36%). The ^1H NMR coupling constants (15.8–16.0 Hz) of the vinyl protons and the IR absorption at $\sim 960\text{ cm}^{-1}$ indicate that the configurations are *E* for the alkenes **2a–2l**. All ^1H and ^{13}C NMR spectra of the alkenes **2a–2l** are consistent with the literature reports.^{6,9,10,27} All spectral data of the hydroximoyl chlorides **3a–3l** are shown below.

2-Phenylbutanohydroximoyl chloride 3a. ^1H NMR (CDCl_3) δ 8.08 (s br, D_2O exchangeable, 1H), 7.39–7.23 (m, 5H), 3.69 (t, *J* 7.6, 1H), 2.16 (dq, *J* 13.8 and 7.6, 1H), 1.90 (dq, *J* 13.8 and 7.6, 1H) and 0.93 (t, *J* 7.6, 3H); ^{13}C NMR (CDCl_3) δ 145.47, 138.97, 128.63, 128.17, 127.51, 54.17, 25.54 and 11.85; GCMS (EI) *m/z* (rel int) 161 (12%), 132 (100), 105 (16) and 77 (41); HRMS (EI) Calc. for $\text{C}_{10}\text{H}_{12}\text{ClNO}$: *M*, 197.0627. Found: M^+ , 197.0617; CIMS (CH_4) 200 [(*M* + 3) $^+$, 20%] and 198 [(*M* + 1) $^+$, 59].

2-(4-Methylphenyl)butanohydroximoyl chloride 3b. ^1H NMR (CDCl_3) δ 8.20 (s br, 1H), 7.25–7.11 (m, 4H), 3.65 (t, *J* 7.6, 1H), 2.33 (s, 3H), 2.12 (dq, *J* 14.8 and 7.6, 1H), 1.87 (dq, *J* 14.8 and 7.6, 1H) and 0.92 (t, *J* 7.6, 3H); ^{13}C NMR (CDCl_3) δ 144.63, 137.16, 135.91, 129.32, 127.97, 53.75, 25.51, 20.97 and 11.85; MS (EI) *m/z* (rel int) 213 [(*M* + 2) $^+$, 33%], 211 (M^+ , 100), 182 (97), 175 (2), 105 (92), 91 (17) and 77 (10); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{14}\text{ClNO}$: *M*(^{37}Cl), 213.0734. Found: M^+ , 213.0751; Calc. *M*(^{35}Cl), 211.0764. Found: M^+ , 211.0767; CIMS (CH_4) 214 [(*M* + 3) $^+$, 4%] and 212 [(*M* + 1) $^+$, 12].

2-(4-Methoxyphenyl)butanohydroximoyl chloride 3c. ^1H NMR (CDCl_3) δ 8.82 (s, 1H), 7.22 (d, *J* 8.6, 2H), 6.88 (d, *J* 8.6, 2H), 3.88 (s, 3H), 3.65 (t, *J* 7.6, 1H), 2.14 (dq, *J* 13.6 and 7.6, 1H), 1.86 (dq, *J* 13.6 and 7.6, 1H) and 0.93 (t, *J* 7.6, 3H); ^{13}C NMR (CDCl_3) δ 158.93, 144.95, 130.92, 129.11, 114.00, 55.20, 53.27, 25.52 and 11.80; GCMS (EI) *m/z* (rel int) 229 [(*M* + 2) $^+$, tr], 227 (M^+ , tr), 191 (15%), 162 (100), 134 (14), 119 (11), 91 (20) and 77 (32); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{14}\text{ClNO}_2$: *M*(^{37}Cl), 229.0683. Found: M^+ , 229.0703; Calc. *M*(^{35}Cl), 227.0713. Found: M^+ , 227.0692.

2-(4-Fluorophenyl)butanohydroximoyl chloride 3d. ^1H NMR (CDCl_3) δ 8.20 (s br, 1H), 7.27–7.23 (m, 2H), 7.04–6.98 (m, 2H), 3.67 (t, *J* 7.6, 1H), 2.12 (dq, *J* 14.6 and 7.6, 1H), 1.86 (dq, *J* 14.6 and 7.6, 1H) and 0.91 (t, *J* 7.6, 3H); ^{13}C NMR (CDCl_3) δ 162.1 (d, *J* 246.3), 144.10, 134.5 (d, *J* 3.7), 129.60 (d, *J* 9.2), 115.5 (d, *J* 22.0), 53.37, 25.63 and 11.84; MS (EI) *m/z* (rel int) 217 [(*M* + 2) $^+$, 17%], 215 (M^+ , 52), 198 (24), 188 (28), 186 (80), 169 (20), 162 (26), 150 (47), 134 (41), 109 (100) and 107 (21); HRMS (EI) Calc. for $\text{C}_{10}\text{H}_{11}\text{ClFNO}$: *M*(^{37}Cl), 217.0484. Found: M^+ , 217.0500; Calc. *M*(^{35}Cl), 215.0539. Found: M^+ , 215.0531.

2-[4-(Trifluoromethyl)phenyl]butanohydroximoyl chloride 3e. ^1H NMR (CDCl_3) δ 8.90 (s br, 1H), 7.59 (d, *J* 8.0, 2H), 7.42 (d, *J* 8.0, 2H), 3.76 (t, *J* 7.4, 1H), 2.18 (dq, *J* 14.6 and 7.4, 1H), 1.91 (dq, *J* 14.6 and 7.4, 1H) and 0.93 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 143.54, 143.02, 129.82 (q, *J* 32.46), 128.51, 125.59 (q, *J* 3.83), 124.09 (q, *J* 272.61), 53.88, 25.44 and 11.70; MS (EI) *m/z* (rel int) 267 [(*M* + 2) $^+$, 5%], 265 (M^+ , 16), 250 (15), 237 (15), 200 (19), 193 (20), 173 (22), 159 (100), 145 (19), 115 (18) and 69 (13); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{11}\text{ClF}_3\text{NO}$:

M(^{37}Cl), 267.0451. Found: M^+ , 267.0466; Calc. *M*(^{35}Cl), 265.0481. Found: M^+ , 265.0479.

2-(2-Methoxyphenyl)butanohydroximoyl chloride 3f. This compound was recrystallized from hexane–ethyl acetate as blocks, mp 114 °C; ^1H NMR (CDCl_3) δ 8.35 (s, 1H), 7.30–7.21 (m, 2H), 7.00–6.87 (m, 2H), 4.25 (t, *J* 7.4, 1H), 3.83 (s, 3H), 2.13 (dq, *J* 14.6 and 7.4, 1H), 1.82 (dq, *J* 14.6 and 7.4, 1H) and 0.93 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 157.38, 144.13, 128.46, 128.12, 127.19, 120.63, 110.75, 55.52, 46.26, 25.20 and 11.80; MS (EI) *m/z* (rel int) 229 [(*M* + 2) $^+$, 27%], 227 (M^+ , 89), 198 (100), 196 (95), 174 (17), 163 (54), 161 (39), 121 (42), 91 (39) and 77 (13); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{14}\text{ClNO}_2$: *M*(^{37}Cl), 229.0684. Found: M^+ , 229.0703; Calc. *M*(^{35}Cl), 227.0713. Found: M^+ , 227.0710 (Calc.: C, 58.03; H, 6.20; N, 6.15%. Found: C, 58.1; H, 6.1; N, 6.2). The X-ray crystal data are listed in Table 2 and the X-ray molecular structure is presented in Fig. 1.

2-(2-Methylphenyl)butanohydroximoyl chloride 3g. ^1H NMR (CDCl_3) δ 8.52 (s, 1H), 7.32–7.16 (m, 4H), 3.95 (t, *J* 7.4, 1H), 2.37 (s, 3H), 2.18 (dq, *J* 14.8 and 7.4, 1H), 1.86 (dq, *J* 14.8 and 7.4, 1H) and 0.93 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 144.33, 136.97, 136.79, 130.61, 127.28, 127.03, 126.34, 49.71, 25.85, 19.56 and 11.82; MS (EI) *m/z* (rel int) 214 [(*M* + 3) $^+$, 15%], 212 [(*M* + 1) $^+$, 51] and 77 (24); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{13}\text{ClNO}$: (*M* – 1), 210.0686. Found: *m/z*, 210.0686.

2-[2-(Trifluoromethyl)phenyl]butanohydroximoyl chloride 3h. This compound was recrystallized from hexane–ethyl acetate as blocks, mp 100–102 °C; ^1H NMR (CDCl_3) δ 8.00 (s br, 1H), 7.70–7.34 (m, 4H), 4.14 (t, *J* 7.4, 1H), 2.23 (dq, *J* 14.8 and 7.4, 1H), 1.85 (dq, *J* 14.8 and 7.4, 1H) and 0.93 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 143.07, 138.27 (q, *J* 1.56), 132.18, 129.07 (q, *J* 29.78), 128.90, 127.45, 126.15 (q, *J* 61.0), 124.29 (q, *J* 275.28), 49.90 (q, *J* 1.92), 27.65 and 11.80; GCMS (EI) *m/z* (rel int) 267 [(*M* + 2) $^+$, tr], 265 (M^+ , tr), 229 (7%), 200 (100), 152 (15), 145 (14), 134 (17) and 95 (5); HRMS (EI) Calc. for $\text{C}_{11}\text{H}_{11}\text{ClF}_3\text{NO}$: *M*(^{37}Cl), 267.0452. Found: M^+ , 267.0454; Calc. *M*(^{35}Cl), 265.0482. Found: M^+ , 265.0479; CIMS (CH_4) 268 [(*M* + 3) $^+$, 5%] and 266 [(*M* + 1) $^+$, 16] (Calc.: C, 49.73; H, 4.17; N, 5.27%. Found: C, 50.4; H, 4.2; N, 5.0). The X-ray crystal data are listed in Table 2, and the X-ray molecular structure is presented in Fig. 2.

2-(2-Thienyl)butanohydroximoyl chloride 3i. ^1H NMR (CDCl_3) δ 7.90 (s br, 1H), 7.23–6.97 (m, 3H), 4.01 (t, *J* 7.4, 1H), 2.13 (dq, *J* 14.2 and 7.4, 1H), 1.98 (dq, *J* 14.2 and 7.4, 1H) and 0.97 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 143.73, 142.01, 126.73, 125.56, 124.68, 48.95, 26.84 and 11.80; MS (EI) *m/z* (rel int) 205 [(*M* + 2) $^+$, 20%], 203 (M^+ , 41), 186 (7), 176 (36), 174 (100), 157 (12), 138 (24) and 97 (17); HRMS (EI) Calc. for $\text{C}_8\text{H}_{10}\text{ClNOS}$: *M*(^{37}Cl), 205.0142. Found: M^+ , 205.0148.

2-(2-Furyl)butanohydroximoyl chloride 3j. ^1H NMR (CDCl_3) δ 8.40 (s br, 1H), 7.37 (dd, *J* 2.0 and 0.8, 1H), 6.34 (dd, *J* 3.4 and 2.0, 1H), 6.23 (dd, *J* 3.4 and 0.8, 1H), 3.84 (t, *J* 7.4, 1H), 2.02 (dq, *J* 14.6 and 7.4, 1H), 2.00 (dq, *J* 14.6 and 7.4, 1H) and 0.96 (t, *J* 7.6, 3H); ^{13}C NMR (CDCl_3) δ 152.19, 142.21, 142.13, 110.35, 107.29, 47.44, 23.62 and 11.44; MS (EI) *m/z* (rel int) 189 [(*M* + 2) $^+$, 1%], 187 (M^+ , 12), 160 (7), 158 (46), 122 (23), 109 (80), 106 (83), 94 (49), 81 (100), 79 (64), 77 (58) and 62 (46); HRMS (EI) Calc. for $\text{C}_8\text{H}_{10}\text{ClNO}$: *M*(^{37}Cl), 189.0370. Found: M^+ , 189.0358; Calc. *M*(^{35}Cl), 187.0400. Found: M^+ , 187.0385.

2,2-Diphenylbutanohydroximoyl chloride 3k. The mp of this compound was 98–100 °C after recrystallization from hexane–ethyl acetate; ^1H NMR (CDCl_3) δ 7.84 (s, 1H), 7.35–7.26 (m, 10H), 2.52 (q, *J* 7.4, 2H) and 0.77 (t, *J* 7.4, 3H); ^{13}C NMR (CDCl_3) δ 146.97, 141.67, 129.49, 127.89, 127.02, 60.08, 32.15 and 9.67; MS (EI) *m/z* (rel int) 275 [(*M* + 2) $^+$, 13%], 273 (M^+ ,

46), 256 (46), 244 (23), 208 (97), 192 (37), 178 (100), 165 (75), 153 (44), 129 (78), 115 (30), 105 (16), 91 (41) and 77 (17); HRMS (EI) Calc. for C₁₆H₁₆ClNO: *M*(³⁷Cl), 275.0891. Found: M⁺, 275.0892; Calc. *M*(³⁵Cl), 273.0921. Found: M⁺, 273.0909 (Calc.: C, 70.20; H, 5.89; N, 5.12. Found: C, 70.4; H, 5.6; N, 5.4%).

2-Methyl-2-phenylbutanohydroximoyl chloride 3l. ¹H NMR (CDCl₃) δ 8.90 (s br, 1H), 7.39–7.21 (m, 5H), 2.24–1.98 (m, 2H), 1.58 (s, 3H) and 0.86 (t, *J* 7.6, 3H); ¹³C NMR (CDCl₃) δ 148.57, 143.64, 128.45, 126.92, 126.42, 51.26, 31.37, 28.60 and 8.62; MS (EI) *m/z* (rel int) 213 [(M + 2)⁺, 30%], 211 (M⁺, 100), 182 (67), 176 (20), 147 (61), 130 (42), 115 (55), 104 (70), 91 (71) and 77 (44); HRMS (EI) Calc. for C₁₁H₁₁ClNO: *m/z*(³⁷Cl), 211.0764. Found: *m/z*, 211.0764, (Calc. for C₁₁H₁₄ClNO: C, 62.41; H, 6.67; N, 6.62. Found: C, 63.4; H, 6.5; N, 6.9%).

Typical procedure for the reaction of β-nitrostyrene with triethylaluminium or diethylaluminium chloride in the presence of MgCl₂ (see Table 3)

β-Nitrostyrene **1a** was slowly added, as described above, to a solution of triethylaluminium or diethylaluminium chloride which contained MgCl₂ (3 equiv.) as the Lewis acid catalyst and under argon. The hydroximoyl chloride **3a** was the major product when the mixture was quenched with ice-cold, conc. hydrochloric acid. The experimental results are shown in Table 3.

Typical procedure for the reaction of β-nitrostyrene with triethylaluminium in the presence of benzoyl peroxide as free-radical initiator (see Table 4)

A 0.1 M diethyl ether solution of β-nitrostyrene **1a** (20 ml, 2 mmol) was added to 5 mmol of triethylaluminium in 30 ml of diethyl ether containing 0.1–2.0 equiv. of benzoyl peroxide and the solution was irradiated with a GE 275W sunlamp and stirred under nitrogen at rt. After the starting material had disappeared, the solution was worked up as described above to obtain, as a single product, the alkene **2a** (Table 4).

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References

- 1 C. D. Bedford and A. T. Nielsen, *J. Org. Chem.*, 1978, **43**, 2460; T. Hayama, S. Tomoda, Y. Takeuchi and Y. Nomura, *Tetrahedron Lett.*, 1983, **24**, 2795; D. Seebach and P. Knochel, *Helv. Chim. Acta*, 1984, **67**, 261; *Tetrahedron*, 1985, **41**, 4861.
- 2 G. D. Buckley, *J. Chem. Soc.*, 1947, 1494; G. D. Buckley and E. J. Ellery, *J. Chem. Soc.*, 1947, 1497; M. S. Ashwood, L. A. Bell, P. G. Houghton and S. H. B. Wright, *Synthesis*, 1988, 379.
- 3 W. Langer and D. Seebach, *Helv. Chim. Acta*, 1979, **62**, 1710.
- 4 A.-T. Hanson and M. Nilsson, *Tetrahedron*, 1982, **38**, 389; S. Stiver and P. Yates, *J. Chem. Soc., Chem. Commun.*, 1983, 50; C. Retherford, M.-C. P. Yeh, I. Schipor, H. G. Chen and P. Knochel, *J. Org. Chem.*, 1989, **54**, 5200; C. Retherford and P. Knochel, *Tetrahedron Lett.*, 1991, **32**, 441; C. Jubert and P. Knochel, *J. Org. Chem.*, 1992, **57**, 5425, 5431.
- 5 A. Pecunioso and R. Menicagli, *Tetrahedron*, 1987, **43**, 5411; *J. Org. Chem.*, 1988, **53**, 45, 2614; 1989, **54**, 2391.
- 6 D. Seebach, H. Schafer, B. Schmidt and M. Schreiber, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1587.
- 7 I. N. N. Namboothiri and A. Hassner, *J. Organomet. Chem.*, 1996, **518**, 69.
- 8 G. A. Russell and C.-F. Yao, *Heteroatom Chem.*, 1992, **3**, 209.
- 9 Y. Han, Y.-Z. Huang and C.-M. Zhou, *Tetrahedron Lett.*, 1996, **37**, 3347.
- 10 C.-F. Yao, C.-M. Chu and J.-T. Liu, *J. Org. Chem.*, 1998, **63**, 719.
- 11 D. H. R. Barton, H. Togo and S. Z. Zard, *Tetrahedron*, 1985, **41**, 5507.
- 12 H. Kunz and K. J. Pees, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1168.
- 13 Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC Web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/277.
- 14 C.-F. Yao, W.-C. Chen and Y.-M. Lin, *Tetrahedron Lett.*, 1996, **37**, 6339; C.-F. Yao, K.-H. Kao, J.-T. Liu, C.-M. Chu, Y. Wang, W.-C. Chen, Y.-M. Lin, W.-W. Lin, M.-C. Yan, J.-Y. Liu, M.-C. Chuang and J.-L. Shiu, *Tetrahedron*, 1998, **54**, 791.
- 15 A. Alexakis, J. Vastra and P. Mangency, *Tetrahedron Lett.*, 1997, **38**, 7745.
- 16 T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, 1960, **82**, 5339.
- 17 M. Christl and R. Huisgen, *Chem. Ber.*, 1973, **106**, 3345.
- 18 G. Kumaran and G. H. Kulkarni, *Tetrahedron Lett.*, 1994, **35**, 5517; *J. Org. Chem.*, 1997, **62**, 1516.
- 19 G. W. Kabalka and R. F. Daley, *J. Am. Chem. Soc.*, 1973, **95**, 4428.
- 20 A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 1968, 1074.
- 21 P. J. Krusic and J. L. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3942.
- 22 P. D. Barlett and T. Funahashi, *J. Am. Chem. Soc.*, 1962, **84**, 2596.
- 23 D. P. Curran, N. A. Porter and B. Giese, in *Stereochemistry of Radical Reactions*, VCH, Weinheim, 1995, pp. 149, 268.
- 24 N. Rabjohn, in *Org. Synth.*, 1963, Coll. Vol. IV, 573.
- 25 F. G. Bordwell and E. W. Garbisch, Jr, *J. Org. Chem.*, 1962, **27**, 3049.
- 26 H. Ohta, N. Kobayashi and K. Ozaki, *J. Org. Chem.*, 1989, **54**, 1802.
- 27 L. A. Paquette and G. D. Maynard, *J. Org. Chem.*, 1989, **54**, 5054; C. Zioudrou, I. Moustakali-Mavridis, P. Chrysochou and G. J. Karabatsons, *Tetrahedron*, 1978, **34**, 3181; B. R. James and C. G. Young, *J. Organomet. Chem.*, 1985, **285**, 321.

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