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Free-Radical Reactions of Trialkylboranes with β-Nitrostyrenes To Generate Alkenes

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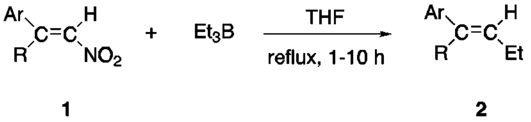
β-Nitrostyrenes **1** react with trialkylboranes under a nitrogen atmosphere to generate high yields of alkenes **2**. The mechanism is proposed to be a free-radical reaction via NO_2/alkyl substitution since the reaction is stimulated by the presence of a trace of oxygen in the nitrogen or *tert*-butyl peroxide or by photolysis and is retarded or inhibited by the addition of galvinoxyl to the solution.

Introduction

Reactions of conjugated nitroalkenes with different kinds of organometallic reagents derived from lithium, magnesium, zinc, aluminum, copper, and boron yielding nitroalkanes or carbonyl compounds have been well studied.[1] It is reported that β-nitrostyrenes react with dialkylzinc,[2] organomanganese,[3] *t*-BuHgX/KI,[4] or trialkylgallium[5] reagents, respectively, to generate alkenes and/or nitroalkanes, and the mechanism is proposed to be an ionic[3] or free-radical reaction.[4,5] Barton has shown that thiopyridone-based esters react with nitroolefins to generate α-nitro sulfides by free radical chain reactions.[6] In the course of our study of the reactions of β-nitrostyrenes with triethylaluminum, not only the ionic products 1-nitro-2-arylbutanes but also the free-radical products 1-aryl-1-butenes were formed in etheral solvent.[7] All these results indicate that conjugated nitroalkenes are useful intermediates in organic synthesis and may react with nonstabilized nucleophiles to generate different products under different workup conditions.[1−7] In this paper, we wish to report the first example of the reactions of the β-nitrostyrenes with trialkylboranes to generate alkenes by alkyl substitution of NO_2.

Results and Discussion

Under refluxing conditions, β-nitrostyrenes **1a**−**l** reacted with triethylborane in THF solvent under a nitrogen atmosphere to generate moderate to high yields (60−100%) of 1-aryl-1-butenes **2a**−**l** (eq 1). All products **2a**−**l** are easily purified by column chromatography due to their low polarity. The configuration of the alkenes is assigned to be the *trans* form according to the NMR spectra.[2,3,5] When isopropyl alcohol was used as the solvent, the yield of **2a** was almost the same as in THF but the reaction time decreased from 10 to 2 h. This result indicates that both isopropyl alcohol and THF can be used as solvent in the free-radical reactions of boranes.[8]



(1)

a: Ar = Ph, R = H
b: Ar = 4-MeC$_6$H$_4$, R = H
c: Ar = 4-MeOC$_6$H$_4$, R = H
d: Ar = 4-FC$_6$H$_4$, R = H
e: Ar = 4-CF$_3$C$_6$H$_4$, R = H
f: Ar = 2-MeOC$_6$H$_4$, R = H
g: Ar = 2-MeC$_6$H$_4$, R = H
h: Ar = 2-CF$_3$C$_6$H$_4$, R = H
i: Ar = 2-thienyl, R = H
j: Ar = 2-furyl, R = H
k: Ar = Ph, R = Ph
l: Ar = Ph, R = Me

This reaction was not successful when β-nitrostyrene (**1a**) reacted with triphenylborane, and only the Michael adduct was isolated when 1-nitro-4-phenyl-1-butene reacted with triethylborane.[2] Only 12% of 2-methyl-1-phenyl-1-butene was generated when 1-phenyl-2-nitropropene reacted with triethylborane under similar conditions. Possible explanations are that the phenyl radical may react with the solvent THF[9] and the reaction is sensitive to steric hindrance of the starting material.[2]

The mechanism is proposed to be a free-radical nonchain reaction involving an addition−elimination process to generate alkenes **2**. This mechanism is obviously different from a literature report that the generation of alkenes proceeds through an ionic addition−migration−elimination pathway.[3] One possibility is that the addition of the ethyl radical generates the benzylic radical, which undergoes β-elimination to yield the final product **2** (Scheme 1).[4,5,10]

The free-radical reaction is obviously stimulated by the presence of a trace of oxygen in the nitrogen,[11] by the

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[1] (a) Seebach, D.; Giorgio, C.; Knochel, P. *Tetrahedron* **1985**, *41*, 4861. (b) Ashwood, M. S.; Bell, L. A.; Houghton, P. G.; Wright, S. G. B. *Synthesis* **1988**, 379. (c) Langer, W.; Seebach, D. *Helv. Chim. Acta* **1979**, *62*, 1710. (d) Pecunioso, A.; Menicagli, R. *J. Org. Chem.* **1989**, *54*, 2391. (e) Jubert, C.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 5431. (f) Shitov, O. P.; Ioffe, S. L.; Leont'eva, L. M.; Tartakovskii, V. A. *J. Gen. Chem. USSR* **1973**, *43*, 1118.

[2] Seebach, D.; Schafer, H.; Schmidt, B.; Schreiber, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1587.

[3] Namboothiri, I. N. N.; Hassner, A. *J. Organomet. Chem.* **1996**, *518*, 69.

[4] Russell, G. A.; Yao, C.-F. *Heteroatom Chem.* **1992**, *3*, 209.

[5] Han, Y.; Huang, Y.-Z.; Zhou, C.-M. *Tetrahedron Lett.* **1996**, *37*, 3347.

[6] Barton, D. H. R.; Togo, H.; Zard, S. Z. *Tetrahedron* **1985**, *41*, 5507.

[7] Yao, C.-F.; Chu, C.-M.; Liu, J.-T.; Kao, K.-H. Manuscript in preparation.

[8] (a) Perrine, J. C.; Keller, R. N. *J. Am. Chem. Soc.* **1958**, *80*, 1823. (b) Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 712.

[9] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

[10] Barton, D. H. R.; Dorchak, J.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1993**, *34*, 8051.

[11] Brown, H. C.; Kabalka, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 714.

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Scheme 1

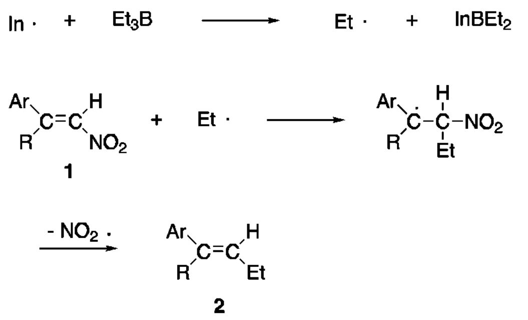


Table 1. Reactions of β-Nitrostyrenes 1 with Et$_3$B in THF under a Nitrogen Atmosphere

compd	condns	product	yield[a] (%)
1a	reflux, 10 h	**2a**	80
1a	reflux, 2 h	**2a**	81[b]
1a	50 °C, 2 h	**2a**	53[c]
1a	10 and % (t-BuO)$_2$, reflux, 2.5 h	**2a**	87
1b	reflux, 2 h	**2b**	100
1b	reflux, 2 h	**2b**	60[d]
1b	50 mol % galvinoxyl, reflux, 2 h	**2b**	0[e]
1c	reflux, 5 h	**2c**	96
1d	reflux, 2 h	**2d**	81
1e	reflux, 2 h	**2e**	84
1f	reflux, 2 h	**2f**	95
1g	reflux, 2 h	**2g**	85
1h	reflux, 2 h	**2h**	89
1i	reflux, 2 h	**2i**	95
1j	reflux, 1 h	**2j**	96
1k	reflux, 2 h	**2k**	90
1l	reflux, 2 h	**2l**	86

[a] Yields (%) were measured by ^{1}H NMR from integrations with a known amount of toluene or dibromomethane as an internal standard. [b] Isopropyl alcohol was used as the solvent. [c] 13% unreacted **1a** was recovered. [d] Under an argon atmosphere and 40% unreacted **1b** was recovered. [e] 91% unreacted **1b** was recovered.

presence of alkyl peroxide,[12] or by photolysis.[8b] With **1b** and under an argon atmosphere, only 60% of **2b** was formed and 40% unreacted starting material **1b** was recovered after the THF solution was refluxed for 2 h. The reaction is also retarded or inhibited by the addition of galvinoxyl, an efficient scavenger for free radicals,[13] to the THF solution. After addition of 50 mol % of galvinoxyl and refluxing for 2 h, no product was formed and only 91% unreacted **1b** was recovered. When 10 mol % of *tert*-butyl peroxide, the free-radical initiator, was added to the **1a** solution, the yield increased and the reaction rate accelerated simultaneously (Table 1).

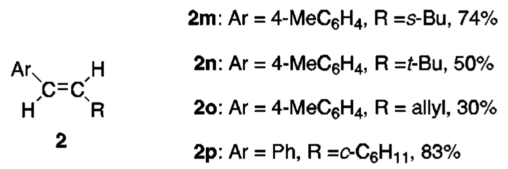
The free-radical reaction also occurs by photolysis. When the THF solution was irradiated with a sunlamp under a nitrogen atmosphere, medium to high yields (52–98%) of alkenes were formed. Both *tert*-butyl peroxide and galvinoxyl had the same effect on the reactions as described above. To substrate **1l** (*trans*), only 54% of product **2l** (*trans*) was generated and 42% of unreacted starting material **1l** recovered even when 10 mol % of *tert*-butyl peroxide was added. This result indicates that the free-radical reaction is very sensitive to steric hindrance in the starting material (Table 2).[2]

Not only triethylborane but also other reagents such as tri-*sec*-butylborane, *B*-*tert*-butyl-9-BBN, or triallylborane react with **1b** in THF solvent and in the presence or absence of *tert*-butyl peroxide under a nitrogen atmosphere to generate alkenes **2m** (reflux 2 h, 74%) and **2n** (1 equiv of peroxide, reflux 3 h, 50%) and diene **20** (reflux 2 h, 30%), respectively. Similarly, 83% of **2p** was also generated when **1a** reacted with tricyclohexylborane under similar condition (reflux 2.5 h).

Table 2. Photolysis of β-Nitrostyrenes 1 with Et$_3$B in THF Solution in the Presence or Absence of *tert*-Butyl Peroxide as Free-Radical Initiator and under a Nitrogen Atmosphere

compd	condns	product	yield[a] (%)
1a	$h\nu$,[b] 2.5 h	**2a**	70
1a	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2a**	78
1b	dark, rt, 2.5 h	**2b**	54[c]
1b	$h\nu$, 2.5 h	**2b**	79[d]
1b	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2b**	96
1b	50 mol % galvinoxyl, $h\nu$, 2.5 h	**2b**	tr[e]
1c	$h\nu$, 4 h	**2c**	79
1c	10 mol % (t-BuO)$_2$, $h\nu$, 4 h	**2c**	96
1d	$h\nu$, 2.5 h	**2d**	67
1d	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2d**	61
1e	$h\nu$, 2.5 h	**2e**	87
1e	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2e**	85
1f	$h\nu$, 3.5 h	**2f**	73
1f	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2f**	69
1g	$h\nu$, 3.5 h	**2g**	65
1g	10 mol % (t-BuO)$_2$, $h\nu$, 3 h	**2g**	62
1h	$h\nu$, 2.5 h	**2h**	90
1h	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2h**	60
1i	$h\nu$, 3.5 h	**2i**	91
1i	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2i**	96
1j	$h\nu$, 2.5 h	**2j**	97
1j	10 mol % (t-BuO)$_2$, $h\nu$, 2.5 h	**2j**	77
1k	$h\nu$, 3 h	**2k**	98
1k	10 mol % (t-BuO)$_2$, $h\nu$, 3 h	**2k**	100
1l	$h\nu$, 3 h	**2l**	52[f]
1l	10 mol % (t-BuO)$_2$, $h\nu$, 3 h	**2l**	54[g]

[a] Yields (%) were measured by ^{1}H NMR from integrations with a known amount of toluene or dibromomethane as an internal standard. [b] Photochemical reactions were performed at ~30 °C at a distance ~35 cm from a 275 W General Electric sunlamp. [c] 28% unreacted **1b** was recovered. [d] 6% unreacted **1b** was recovered. [e] 85% unreacted **1b** was recovered. [f] 33% unreacted **1l** was recovered. [g] 42% unreacted **1l** was recovered.



The free-radical substitution of the nitro group of the β-nitrostyrenes **1a**–**l** to the alkenes **2a**–**p** described herein is remarkable for the following reasons: (1) Usually the nitro group is a good activator for Michael addition[14] and acts as a leaving group only in special cases.[15] (2) Vinylic C–C coupling is usually carried out with sensitive organometallic reagents and halides and normally requires a catalyst such as Pd or Ni.[16] Since the β-nitrostyrenes **1a**–**l** leading to the alkenes **2a**–**p** are

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[12] (a) Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387. (b) Brown, H. C.; Midland, M. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 1024.

[13] Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.

[14] (a) Nitroalkanes and Nitroalkenes in Synthesis. *Tetrahedron* **1990**, *46*, 7313. (b) Barett, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95.

[15] (a) Tamura, R.; Kamimura, A.; Ono, N. *Synthesis* **1991**, 423. (b) Kornblumm, N. *Aldrichim. Acta* **1990**, *23*, 71. (c) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. *Chimia* **1979**, *33*, 1 and references therein.

[16] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 14.4–14.5, pp 710–727. (b) Heck, R. F. In *Palladium in Organic Synthesis*; Academic Press: New York, 1985.

more accessible (aldehyde and nitromethane) than the corresponding vinyl halides or metal derivatives, the method described here is superior to many well-established procedures for the synthesis of alkenes, which often lead to mixtures of *cis*- and *trans*-isomers.[17]

Conclusion

In conclusion, we have described a novel radical reaction between trialkylboranes and β-nitrostyrenes via NO_2/alkyl substitution. This not only gives a useful synthetic method of (*E*)-olefins but also represents the first example of reaction of organoboranes with α,β-unsaturated nitroolefins. The reaction would broaden the scope of utility of organoboranes reagents in organic synthesis.

Experimental Section

General Methods. All reactions were performed in flame- or oven-dried glassware under a positive pressure of nitrogen. Air- and moisture-sensitive compounds were introduced by the use of a syringe or cannula through a rubber septum. Compounds **1a**−**e**, **1i**, triethylborane, tri-*sec*-butylborane, and *B-tert*-butyl-9-BBN were purchased from Aldrich. Compounds **1f**−**h**,[18] **1j**,[19] **1k**,[20] **1l**,[21] triallylborane,[22] and tricyclohexylborane[22] were prepared according to or by modifying the literature procedures. Products **2a**−**d**,**i**, **2j**,[2,6] **2l**,[23] and **2p**[6] are consistent with literature reports. THF was distilled from sodium/benzophenone ketyl under an argon atmosphere. THF and isopropyl alcohol were degassed prior to reactions. Analytical thin-layer chromatography was performed with E. Merck silica gel 60F 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, MS or HRMS were measured with a JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL Ex-400 or Varian Gemini-200. All NMR data were obtained in $CDCl_3$ solution, chemical shifts (δ) are given in ppm relative to TMS, and *J* values are given in Hz.

Typical Experimental Procedure. A solution of 2.0 mmol of 1-(2-methoxyphenyl)-2-nitroethene (**1f**) in 25 mL of THF was treated with 6 mmol of 1.0 M Et_3B solution in THF, and the solution was kept gently refluxing under a nitrogen atmosphere. After 2 h, the solvent was evaporated to obtain an oily mixture. The crude NMR analysis indicated the mixture contained 95% yield of **2f** by using toluene as an internal standard. Flash column chromatography was used to purify the mixture by using hexane as the eluent to obtain the least polar product **2f**. After most of the solvent was evaporated, the residue was further dried at ca. 1.0 Torr for 5 min to give pure **2f**. All the experimental results are shown in Table 1.

***trans*-1-[4-(Trifluoromethyl)phenyl]-1-butene (2e):** ^1H NMR ($CDCl_3$) δ 7.52 (d, 2H, $J = 8.4$), 7.39 (d, 2H, $J = 8.4$), 6.45−6.27 (m, 2H), 2.31−2.18 (m, 2H), 1.09 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 141.55 (q, $J = 1.2$), 135.50, 128.69 (q, $J = 32.5$), 127.76, 126.08, 125.46 (q, $J = 3.8$), 124.43 (q, $J = 272.6$), 26.02, 13.25; GCMS (EI) *m/z* (relative intensity) 200 (M^+, 64), 185 (71), 165 (59), 131 (100), 115 (47), 91 (22), 69 (26); HRMS (EI) calcd for $C_{10}H_{11}F_3$ 200.0813, found 200.0817; CIMS (CH_4) 201 ($(M + 1)^+$, 27).

***trans*-1-(2-Methoxyphenyl)-1-butene (2f):** ^1H NMR ($CDCl_3$) δ 7.40 (dd, 1H, $J = 7.6$, 1.8), 7.16 (dt, 1H, $J = 8.0$, 1.8), 6.93−6.79 (m, 2H), 6.71 (dt, 1H, $J = 16.0$, 1.4), 6.24 (dt, 1H, $J = 16.0$, 6.4), 3.80 (s, 3H), 2.24 (quint d, 1H, $J = 7.4$, 1.4), 1.09 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 156.33, 133.31, 127.75, 127.03, 126.37, 123.42, 120.62, 110.74, 55.29, 26.39, 13.64; GCMS (EI) *m/z* (relative intensity) 162 (M^+, 62), 147 (18), 131 (35), 115 (40), 91 (100), 77 (30); HRMS (EI) calcd for $C_{11}H_{14}O$ 162.1045, found 162.1043; CIMS (CH_4) 163 ($(M + 1)^+$, 12).

***trans*-1-(2-Methylphenyl)-1-butene (2g):** ^1H NMR ($CDCl_3$) δ 7.43−7.08 (m, 4H), 6.56 (d, 1H, $J = 15.8$), 6.12 (dt, 1H, $J = 15.8$, 6.4), 2.31 (s, 3H), 2.27−2.16 (m, 2H), 1.09 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 137.08, 134.90, 133.99, 130.16, 126.74, 126.67, 126.02, 125.44, 26.32, 19.71, 13.72; GCMS (EI) *m/z* (relative intensity) 146 (M^+, 43), 131 (100), 115 (42), 104 (14), 91 (52), 77 (17); HRMS (EI) calcd for $C_{11}H_{14}$ 146.1095, found 146.1097.

***trans*-1-[2-(Trifluoromethyl)phenyl]-1-butene (2h):** ^1H NMR ($CDCl_3$) δ 7.62−7.23 (m, 4H), 6.76 (d, 1H, $J = 16.0$), 6.21 (dt, 1H, $J = 16.0$, 6.6), 2.34−2.19 (m, 2H), 1.10 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 137.23 (q, $J = 1.56$), 136.91, 131.73 (q, $J = 0.76$), 127.23, 127.05 (q, $J = 29.76$), 126.52, 125.57 (q, $J = 57.46$), 125.01 (q, $J = 1.92$), 124.56 (q, $J = 274.88$), 26.20, 13.26; GCMS (EI) *m/z* (relative intensity) 200 (M^+, 57), 185 (58), 165 (57), 151 (25), 131 (100), 115 (36), 91 (21), 69 (33); HRMS (EI) calcd for $C_{11}H_{11}F_3$ 200.0813 found, 200.0810; CIMS (CH_4) 201 ($(M + 1)^+$, 56).

1,1-Diphenyl-1-butene (2k): ^1H NMR ($CDCl_3$) δ 7.40−7.19 (m, 10H), 6.11 (t, 1H, $J = 7.4$), 2.16 (quint, 2H, $J = 7.4$), 1.07 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 142.91, 141.08, 140.35, 131.77, 129.96, 128.17, 128.10, 127.27, 126.88, 126.79, 23.13, 14.43; MS (EI) *m/z* (relative intensity) 208 (M^+, tr), 193 (5), 183 (70), 167 (100), 165 (59), 152 (27), 105 (26), 77 (23); HRMS (EI) calcd for $C_{15}H_{16}$ 208.1252, found 208.1249.

***trans*-2-Phenyl-2-pentene (2l):**[23] ^1H NMR ($CDCl_3$) δ 7.40−7.15 (m, 5H), 5.77 (tq, 1H, $J = 6.0$, 1.4), 2.30−2.20 (m, 2H), 2.02 (dt, 3H, $J = 1.4$, 0.8), 1.05 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 144.03, 134.10, 130.28, 128.16, 126.46, 125.61, 21.97, 15.49, 13.99; GCMS (EI) *m/z* (relative intensity) 146 (M^+, 40), 131 (100), 115 (32), 103 (12), 91 (69), 77 (27); HRMS (EI) calcd for $C_{11}H_{14}$ 146.1096, found 146.1086.

***trans*-1-(4-Methylphenyl)-3-methyl-1-pentene (2m):** ^1H NMR ($CDCl_3$) δ 7.24 (d, 2H, $J = 8.2$), 7.08 (d, 2H, $J = 8.2$), 6.30 (d, 1H, $J = 16.0$), 6.45 (dd, 1H, $J = 16.0$, 7.6), 2.31 (s, 3H), 2.21 (m, 1H), 1.39 (quint, $J = 7.2$), 1.06 (d, 3H, $J = 6.6$), 0.90 (t, 3H, $J = 7.4$); ^{13}C NMR ($CDCl_3$) δ 136.42, 135.77, 135.29, 129.17, 128.02, 125.89, 38.79, 29.78, 20.98, 20.13, 11.69; GCMS (EI) *m/z* (relative intensity) 174 (M^+, 80), 159 (14), 145 (100), 130 (10), 115 (12), 91 (7), 77 (3); HRMS (EI) calcd for $C_{13}H_{18}$ 174.1409, found 174.1402.

***trans*-1-(4-Methylphenyl)-3,3-dimethyl-1-butene (2n):** ^1H NMR ($CDCl_3$) δ 7.24 (d, 2H, $J = 8.0$), 7.07 (d, 2H, $J = 8.0$), 6.28 (d, 1H, $J = 16.0$), 6.17 (d, 1H, $J = 16.0$), 2.30 (s, 3H), 1.10 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 140.88, 136.39, 135.37, 129.20, 125.98, 124.51, 33.19, 29.61, 21.00; GCMS (EI) *m/z* (relative intensity) 174 (M^+, 84), 159 (100), 144 (8), 131 (11), 117 (6), 105 (11), 91 (5), 77 (2), 57 (8); HRMS (EI) calcd for $C_{12}H_{15}$ ($M - CH_3$) 159.1173, found 159.1175.

***trans*-1-(4-Methylphenyl)-1,4-pentadiene (2o):** ^1H NMR ($CDCl_3$) δ 7.24 (d, 2H, $J = 8.2$), 7.10 (d, 2H, $J = 8.2$), 6.38 (d, 1H, $J = 16.0$), 6.16 (dt, 1H, $J = 16.0$, 6.4), 5.16−5.02 (m, 2H), 6.00−5.80 (m, 1H), 2.95 (tq, 2H, $J = 6.4$, 1.6), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 136.78, 136.72, 134.94, 130.77, 129.24, 127.18, 125.99, 115, 54, 36.93, 21.03; GCMS (EI) *m/z* (relative inten-

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[17] (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev. (Washington, D.C.)* **1989**, *89*, 863. (b) Boutagy, R.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87. (c) Heck, R. F. *Org. React.* **1982**, *27*, 345. (d) Ager, D. J. *Org. React.* **1990**, *38*, 1. (e) Hassner, A.; Stumer, B. Organic Synthesis based on Name Reactions and Unnamed Reactions. *Tetrahedron*; Organic Chemistry Series, Vol. 11, Elsevier: New York, 1994; and references therein.

[18] Rabjohn, N. In *Organic Syntheses*, 2nd ed.; Blatt, A. H., Ed.; John Wiley & Sons: New York, 1963; Collect. Vol. IV, p 573.

[19] Bourguignon, J.; Nard, G. L.; Queguiner, G. *Can. J. Chem.* **1985**, *23*, 2354.

[20] Bordwell, F. G.; Garbisch, E. W., Jr. *J. Org. Chem.* **1962**, *27*, 3049.

[21] Ohta, H.; Kobayashi, N.; Ozaki, K. *J. Org. Chem.* **1989**, *54*, 1802.

[22] Brown, H. C.; Racherla, U. S. *J. Org. Chem.* **1986**, *51*, 427.

[23] (a) Paquette, L. A.; Maynard, G. D. *J. Org. Chem.* **1989**, *54*, 5054. (b) Zioudrou, C.; Moustakali-Mavridis, I.; Chrysochou, P.; Karabatsos, G. J. *Tetrahedron* **1978**, *34*, 3181. (c) James, B. R.; Young, C. G. *J. Organomet. Chem.* **1985**, 285, 321.

sity) 158 (M^+, 100), 143 (85), 128 (47), 115 (26), 105 (15), 91 (12), 77 (6); HRMS (EI) calcd for $C_{12}H_{14}$ 158.1095, found 158.1089.

Typical Procedure for the Reactions of *β*-Nitrostyrenes with Triethylborane in the Presence or Absence of *tert*-Butyl Peroxide as Free-Radical Initiator. A solution of 1-(2-methoxyphenyl)-2-nitroethene (**1f**) (2.0 mmol) in the presence or absence of 10 mol % of *tert*-butyl peroxide in 25 mL of THF was treated with 6 mmol of 1.0 M Et_3B solution in THF, and then the solution was irradiated with a GE 275W sunlamp at ~30 °C at a distance ~35 cm and stirred under a nitrogen atmosphere. After the starting material disappeared, the solution was worked up as described above to obtain as a single product the alkene **2f**. All the experimental results are shown in Table 2.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of compounds **2a**−**p** (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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