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Conjugate Addition of an Allylzinc Reagent to ß-Nitrostyrenes

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Abstract : **ß-Nitrostyrenes undergo conjugate addition with an allylzinc reagent in dry DMF at room temperature.** © 1999 Published by Elsevier Science Ltd. All rights reserved.

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Conjugated nitroalkenes are excellent Michael acceptors giving synthetically useful products[1-4] and we report here the conjugate addition of an allylzinc reagent to ß-nitrostyrenes.

1-Nitro-2-arylpent-4-enes were obtained in high yields by conjugate addition of an allylzinc[5] reagent to a variety of ß-nitrostyrenes. The allylzinc reagent (generated *in situ*), was allowed to react with ß-nitrostyrenes in dry DMF at ambient temperature (25°C) under a nitrogen atmosphere. High conversions could be achieved by monitoring the reaction progress by TLC and the products were isolated by quenching the reaction with aqueous ammonium chloride followed by solvent extraction, see table. High conversion can be achieved within one hour in the case of many nitrostyrenes bearing electron donating groups on the aromatic ring. However, comparatively long reaction times of 3-4.5 hrs were required to achieve high yields with substrates having electron withdrawing groups or bulky aromatic groups. The conversions are generally clean, exclusively giving 1-nitro-2-arylpent-4-enes, if the reactions are conducted under anhydrous conditions (N_2 atmosphere and dry DMF as solvent). However it was observed that whenever commercial DMF with moisture (5-8% water) was used as solvent, the corresponding homoallylalcohols were isolated in significant quantities. This may be attributed to the concomitant cleavage of nitrostyrenes in presence of water into aldehydes which, in turn, become substrates for the allylzinc addition. Thus, careful exclusion of moisture is mandatory in order to achieve high yields of 1-nitro-2-arylpent-4-enes.

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Scheme

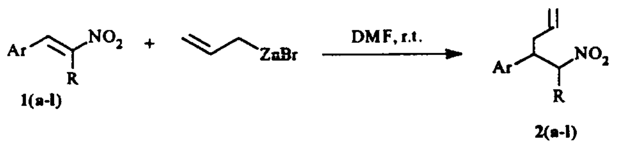

Table : Conjugate addition of Allylzinc Bromide to ß-Nitrostyrenes

Entry	Ar	R	Reaction Time (h.)	Yield[a] (%)
a.	Phenyl	H	1.5	83
b.	Phenyl	CH_3	1.5	80
c.	Piperonyl	H	0.5	86
d.	Piperonyl	CH_3	0.5	82
e.	4-Chlorophenyl	H	3.0	80
f.	4-Methoxyphenyl	H	0.5	90
g.	4-Methylphenyl	H	0.5	85
h.	3,4-Dimethoxyphenyl	H	1.0	88
i.	3,4-Dichlorophenyl	H	3.5	76
j.	Naphthyl	H	3.5	78
k.	Anthracenyl	H	4.5	75
l.	Thienyl	H	0.5	85

a) Isolated yields after column chromatography.

In conclusion, we present here a convenient method for obtaining a variety of 1-nitro-2-arylpent-4-enes through addition of an allylzinc reagent to ß-nitrostyrenes.

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References & Notes

[1] a) Barrett AGM, Graboski GG. Chem. Rev. 1986, 86: 751. b) Barrett AGM, Nitroalkanes and Nitroalkenes in Synthesis. Tetrahedron Symposia-in-print. Tetrahedron. 1990, 46: 7313

[2] a) Menicagli R, Samaritani S, Tetrahedron. 1996, 52: 1425. b) Yao CF, Chen WC, and Lin YM, Tetrahedron Lett. 1996, 37: 6339. c) Ashwood MS, Bell LA, Houghton PG, Wright SHB. Synthesis. 1988, 379.

[3] Ochiai M, Arimoto M, Fujita E. Tetrahedron Lett. 1981, 22: 1115. b) Hwu JR, Wang N. Synth. Commun. 1988, 18: 21 c) Tsay SC, Patel HV, Hwu JR, Synlett., 1998, 9: 939. d) Cormier RA, Norris TE. Synth. Commun. 1987, 17: 1673.

[4] Pecunioso A. and Menicagli R. J. Org. Chem. 1989, 54: 2191.

[5] **Typical Procedure** : Allylzinc bromide was prepared by stirring activated zinc powder[6] (1.3 g, 20 mmol) and allyl bromide (2.4 g, 20 mmol) in dry DMF (10 ml) for 20 minutes at room temperature and then added slowly to a solution of *p*-methyl-ß-nitrostyrene (1.6 g, 10 mmol) in dry DMF (10 ml). The resulting reaction mixture was stirred at room temperature under a N_2 atmosphere for 30 min. After complete conversion, as indicated by TLC, the reaction mass was quenched with aqueous ammonium chloride (10%, 20 ml) and extracted with ethyl acetate (2 x 25 ml). The combined organic layer was washed with brine (20 ml), dried over anhydrous Na_2SO_4 and concentrated to obtain the crude product, which was purified by column chromatography on silicagel (Aldrich, 100-200 mesh, ethyl acetate - hexane, 1:9) to afford **2g** (1.7 g, 85% yield) as pale yellow oil. ^1H NMR ($CDCl_3$) : δ 6.9-7.15 (m, 4H), 5.45-5.65 (m, 1H), 4.9-5.05 (m, 2H), 4.35-4.55 (m, 2H), 3.35-3.5 (m, 1H), 2.25-2.4 (m, 2H), 2.2 (s, 3H).

[6] Commercially available zinc was activated by washing with 5% HCl, water, acetone, dry ether and drying in vacuum at 100°C. Newman MS, Evans FJ, J. Am. Chem. Soc. 1955, 77: 946.