Pergamon

Tetrahedron Letters 39 (1998) 2695–2696

TETRAHEDRON
LETTERS

One-Pot Synthesis of Nitroolefins Using Zeolite.

R. Sreekumar* [a], Raghavakaimal Padmakumar [b] and P. Rugmini [b]

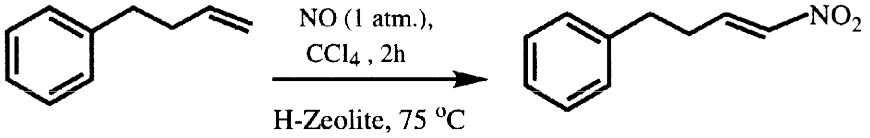
[a] *Department of Physiology, University of Wisconsin, Madison, USA.*
[b] *Department of Chemistry &Biochemistry, University of Nebraska, Lincoln, USA.*

Received 29 September 1997; accepted 11 February 1998

Abstract: Nitroolefins, versatile intermediates in organic synthesis, are conveniently prepared in good yields by nitration of olefins using nitric oxide and zeolite as described. © 1998 Elsevier Science Ltd. All rights reserved.

In recent years, there has been a tremendous resurgence of interest in various selective organic transformations mediated by zeolites.[1,2] Nitroalkenes are an important class of compounds in organic synthesis, as powerful electrophiles that readily undergo conjugate addition reactions with nucleophiles or radicals and as potent dienophiles in the Diels-Alder reactions. In addition, the nitro group is particularly interesting in synthesis since it can be transformed into a variety of diverse functionalities.[3] Nitroalkenes are prepared either from aldehydes and ketones or from alkenes itself.[4] Although the reaction of nitric oxide with olefins has already been reported, the reaction conditions were rather severe to form several undesirable by-products, and yields and selectivities of nitroolefins were not satisfactory.[5] However, no report is available in the literature in which a zeolite is employed to promote the conversion of olefins to the corresponding nitroolefins.

In this communication, we wish to report a convenient and simple heterogeneous catalytic method for the synthesis of nitroolefins from various olefins with nitric oxide under mild conditions using HY-Zeolite and HEMT (hexagonal analog of faujasite-type zeolite).



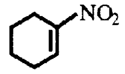
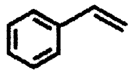
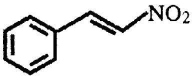
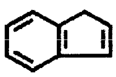
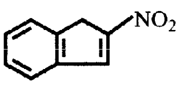
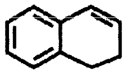
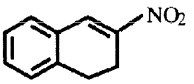
The olefins were purchased from Aldrich or Fluka chemical Co. and zeolites (Y-Zeolite and EMT) were synthesized as reported elsewhere.[6] Prior to use, zeolites were calcined at 500 °C for 5h in the presence of air. The reaction on HY-Zeolite was optimized with respect to temperature, reaction time and catalyst to substrate ratio.

A typical procedure is described for the nitration of 4-phenyl-1-butene; the R.B.flask containing a solution of olefin (132 mg, 1.0 mmol) in CCl_4 (25 mL) and HY-Zeolite (2.0 g) was evacuated and filled with nitric oxide gas (1.0 atmospheric pressure). Then the solution was stirred at 75 °C for 2 h. The reaction mixture was filtered after 2h through a Celite pad and the zeolite was washed with CCl_4 (3 x 25 mL), followed by

PII: S0040-4039(98)00408-0

removal of CCl_4 and purification furnished 1-nitro-4-phenyl-1-butene in 81% yield. This methodology has been successfully applied for the conversion of other olefins over HY-Zeolite and HEMT to the corresponding nitroolefins and the results are summarized in Table 1.

Table 1. Comparison of the yields of various nitroolefins over HY-Zeolite and HEMT.

			Yield[a]	
Entry	Substrates	Products[b]	HY-Zeolite	HEMT
1			78	74
2			80	72
3			71	68
4			79	72
5			81	75
6			68	65
7			76	70

[a] Yield of isolated pure product. [b] satisfactory NMR, IR and Mass spectral datas were obtained.

In summary, we have established a facile heterogeneous catalytic method for the conversion of olefins to the corresponding nitroolefins in good yield. The positive features of these inexpensive zeolites includes ease of work up and separation of the product, lack of corrosiveness and other environmental hazards, regeneration and reuse of the catalyst.

References

1. a) Martens, J. A.; Souverijns, W.; Froment, G. F.; Jacobs, P. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2528. b) Dartt, C.B.; Davis, M. E. *Catal. Today* **1994**, *19*, 151.
2. a) Holderich, W.; Hesse.; Naumann, F. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 226.
   b) Sreekumar, R.; Murthy, Y. V. S. N.; Pillai, C.N. *J. Chem. Soc. Chem.Commun.* **1992**, 1624.
   c) Sreekumar, R.; Padmakumar, R.*Tetrahedron Lett.* **1996**, 30, 5281.
   d) Sreekumar, R. Padmakumar, R and Rugmini, P. *Chem. Comm.* **1997**, 1133.
3. a) Barrett, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95 . b) Barrett, A. G. M. *Chem. Rev.* **1986**, *86*, 751.
4. a) Rajappa, S. *Tetrahedron* **1981**, *37*, 1453. b) Perekalin, V. V. *J.Org. Chem. USSR* **1985**, *21*, 1011. c) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733. d) Seebach, D.; Calderari, G.; Knochel, P. *Tetrahedron* **1985**, *41*, 4861.
5. Brown, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 2480. b) Philips Petroleum Co., *U. S. Patent 3658922*, **1972**.
6. Dougnier, F.; Patarin, J.; Guth, J. L.; Anglerot, D. *Zeolites* **1992**, *12*, 160 .