

Envirocat EPZG^R as a New Heterogenous Catalyst for the Efficient Synthesis of Conjugated Nitroolefins

B.P.Bandgar,* M.B. Zirange, P.P. Wadgaonkar

Dept. of Chem., P.G. and Research Centre, R.B.N.B. College, Shirampur-413709, M.S., India. Fax : 0091-2422-23665

Received 25 October 1995

Abstract : A new, simple and practical procedure for direct transformation of aldehydes and nitroalkanes into conjugated nitroolefins in the absence of a solvent by using Envirocat EPZG^R as a heterogenous catalyst has been described.

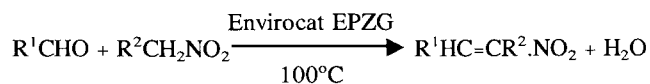
Nitroalkenes were found to be important because of their biological activity such as insecticide,^{1,2} fungicide,^{1,3} and pharmacologically valuable substances⁴. They have proved to be valuable precursors to a wide variety of target molecules. The utility of nitroalkenes in organic synthesis is largely due to their conversion into a variety of functionalities.^{5,6} Alternatively they are powerful dienophiles in Diels-Alder reactions and readily undergo addition reactions with many different nucleophiles.⁶ A few nitroolefins also occur in nature.⁷

The classical preparation of nitroolefins involves the Henry condensation reaction followed by dehydration of the resultant β -nitro alcohols.⁸ For this purpose several reagents have been used.⁹⁻¹¹ In continuation of our interest in the use of heterogenous catalyst for organic transformation,¹² we report herein rapid one step synthesis of conjugated nitroolefins from aldehydes and nitroalkanes by using Envirocat EPZG^R as a novel heterogenous catalyst.

In recent years, there has been a considerable growth in interest in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials.¹³ Envirocat^R, a new family of supported reagents is a breakthrough in an environmentally friendly chemistry.¹⁴ These reagents are non-toxic powders which can be filtered easily from the process and may be reused several times before they are exhausted. These supported reagents are capable of catalyzing Friedel-Crafts alkylation and acylation, sulfonylation, oxidation and other related processes. Envirocat EPZG^R is one of the such solid supported catalyst which exhibits both Bronsted and Lewis acid characteristics.¹⁴

Envirocat EPZG^R was activated 1 h prior to use by azeotropic drying. The synthesis of nitroolefins was carried in the absence of a solvent by heating a mixture of aldehyde and nitroalkane at 100°C for the specified time. The results are summarized in the table. The products were obtained in excellent yields with exclusively (E)-geometry¹¹ of the newly formed double bond and no contamination with the corresponding (Z)-isomers.¹¹

In conclusion, the use of Envirocat EPZG^R as a heterogenous catalyst for the synthesis of conjugated nitroolefins from aldehydes and nitroalkanes is a viable alternative to the existing procedures. Furthermore, this method is advantageous because of rapid solvent-free reactions, easy isolation of products in high yields by simple filtration and recyclability of the catalyst.



Typical procedure for the synthesis of conjugated nitroolefin. A Mixture of benzaldehyde (5 mmol), nitroethane (5 mmol) and Envirocat EPZG^R (100 mg) was heated at 100°C with constant stirring for 30 minutes; while monitoring the reaction by TLC. Then the mixture was cooled to room temperature and treated with dichloromethane (10 ml). Envirocat EPZG^R

Table. Synthesis of conjugated nitroolefins catalyzed by Envirocat EPZG^R

Entry	R ¹	R ²	Reaction Time (min)	Yield ^{a,b} %
1	n-C ₆ H ₁₃	H	20	94
2	2-Furfuryl	H	18	90
3	C ₆ H ₅	H	25	93
4	4-Cl.C ₆ H ₄	H	22	91
5	4-MeO.C ₆ H ₄	H	25	90
6	C ₆ H ₅	Me	30	97
7	2-Furfuryl	Me	15	95
8	4-Cl.C ₆ H ₄	Me	25	92
9	4-MeO.C ₆ H ₄	Me	21	91
10	Me(CH ₂) ₁₅ CH ₂	Me	15	93
11	PhCH ₂ CH ₂	Me	20	95

a. Isolated yields of pure products.

b. Products are characterized by I.R., ¹H NMR, ¹³C NMR and comparison with authentic samples.

was removed by filtration and washed with dichloromethane (3 x 10 ml). Removal of the solvent under reduced pressure gave the product in almost pure form (97%).

Acknowledgement. We thank Contract Chemicals, England for the generous gift of Envirocat EPZG^R, Mr. Sushil Gangwal and Mr. Vishnu Halnor for recording the spectra.

References and Notes

R : Registered trade mark of Contract Chemicals, England.

- Bousquet, E.W.; Kirby, J.E.; Searle, N.E.; U.S. Patent 2335384, 1943; *Chem. Abstr.* **1944**, 3834.
- Brown, A.W.; Robinson, D.B.W.; Hurtig, H.; Wenner, B.J. *Can. J. Res.* **1948**, *26D*, 177.
- Brian, P.W.; Grove, J.F.; McGowan, J.C. *Nature* **1946**, *158*, 876; McGowan, J.C.; Brian, P.W.; Hemming, H.G. *Ann. Appl. Biol.* **1948**, *35*, 25; Bocobo, F.C.; Curtis, A.C.; Block, W.D.; Harrell, E.R.; Evans, E.E.; Haines, R.F. *Antibiot. Chemother.* **1956**, *66*, 385.
- Schales, O.; Graefe, H.A. *J. Am. Chem. Soc.* **1952**, *74*, 4486; Dann, O.; Moller, E.F. *Chem. Ber.* **1949**, *82*, 76; Harker, R.J. U.S. Patent 2889 2436, 1959; *Chem. Abstr.* **1959**, *53*, 17414i; Zee-Cheng, K.; Cheng, C. *J. Med. Chem.* **1969**, *12*, 157.
- Ballini, R.; Bosica, G. *Synthesis* **1994**, 723.
- Barrett, A.G.M.; Graboski, G.G. *Chem. Rev.* **1986**, *86*, 751; Kabalka, G.W.; Varma, R.S. *Org. Prep Proc. Int.* **1987**, *19*, 283; Barrett, A.G.M. *Chem. Soc. Rev.* **1991**, *20*, 95.
- Bauer, H.H.; Urbas, L. *In the Chemistry of the Nitro and Nitroso Group Parts 1 and 2*; Feuer, H. Patai; S., Ed.; Wiley Interscience: New York 1969/70; Stermitz, F.R.; Norris, F.A.; Williams, M.C.; *J. Am. Chem. Soc.* **1969**, *91*, 4599; Vrkov, J.; Ubik, K. *Tetrahedron Lett.* **1974**, 1463.

8. Henry, L. C. R. *Acad. Sci.* **1895**, 120, 1265.
9. Ranganathan, D.; Bhusan Rao, C.; Ranganathan S.; Mehrotra, A. K.; Iyenger, R. *J. Org. Chem.* **1980**, 45, 1885; Knochel, P.; Seebach, D. *Synthesis* **1982**, 1017; Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, 40 2138; Knochel, P.; Seebach, D. *Tetrahedron Lett.* **1982**, 23, 3897; Seebach, D.; Knochel, P. *Hel. Chim. Acta* **1984**, 67, 261.
10. Balini, R.; Chatagnani, R.; Petrini, M., *J. Org. Chem.* **1992**, 57, 2160.
11. Saikia, A.; Barua, N.C.; Sharma, R.P.; Ghosh, A.C. *Synthesis* **1994**, 685.
12. Bandgar, B. P. ; Aghade, B. B.; Jagtap, S. R.; Wadgaonkar, P.P., *Synth. Commun.* **1995**, 25, 2211.
13. Clark, J.H.; Kybett, A.P.; Macquarrie, D.J. *Supported Reagents*, VCH, New York, 1992.
14. Envirocat EPZG^R was supplied by Contract Chemicals, Penrhyn Road, Knowsley Industrial Park South, Prescott, Merseyside, England. Information about Envirocat EPZG^R was obtained from *Envirocats-Supported Reagents: Product Information of Contract Chemicals, England*.