Tetrahedron Letters, Vol.32, No.29, pp 3579-3582, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

Highly Selective Reduction of Conjugated Nitroalkenes with Zinc Borohydride in DME

Brindaban C. Ranu* and Rupak Chakraborty

Department of Organic Chemistry, Indian Association for the
Cultivation of Science, Jadavpur, Calcutta - 700 032, India

Key Words: Zinc borohydride; reduction of nitroalkenes; oximes; nitroalkanes

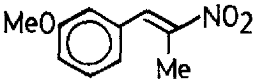
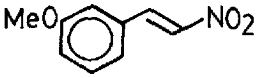
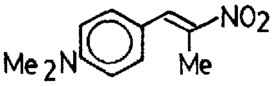
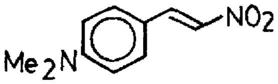
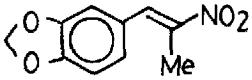
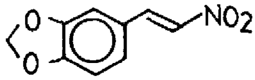
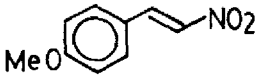
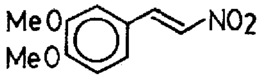
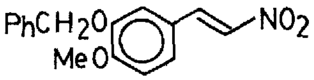
Abstract: Zinc borohydride in 1,2-dimethoxyethane reduces α-substituted conjugated nitroalkenes to the corresponding oximes and non-α-substituted ones to the corresponding nitroalkanes in excellent yields.

Nitroalkenes are of great synthetic potential in organic chemistry.[1] The reduction of conjugated nitroalkenes provides easy access to a variety of functionalities, e.g. nitroalkanes, amines, oximes, hydroxylamines etc.[2,3] However, reduction of nitroalkenes *with hydride reducing agents is capricious. For instance, lithium aluminium hydride* leads to a mixture of products containing saturated amine, nitroalkane, oxime and hydroxylamine,[2,4] whereas sodium borohydride produces the corresponding nitroalkanes.[5] In light of these results, our recent endeavour of selective reductions using zinc borohydride[6] prompted us to investigate the reduction of nitroalkenes also. Very interestingly, we have observed that α-substituted conjugated nitroalkenes are reduced by zinc borohydride in DME[7] to the corresponding oximes, whereas those having no α-substitution simply produced the corresponding nitroalkanes.

In a typical procedure, the nitroalkene[8] (1 mmol)[9] was stirred with zinc borohydride (1 mmol) in DME at 0-5°C.[10] After completion (monitored by TLC) the reaction mixture was decomposed with H_2O and extracted with ether. Evaporation of solvent left the crude product which was then purified by crystallization or column chromatography. The results are reported in Table-1.

As shown in Table-1, several structurally varied conjugated nitroalkenes were reduced with zinc borohydride in DME. In general, α-substituted nitroolefins (entries 1-4,6,8,10) produced the corresponding ketoximes and those having no substitution at the α-position (entries 5,7,9,11-14) underwent clean reductions to the corresponding nitroalkanes in excellent yields. Interestingly, in neither case mixed product of oxime and nitroalkane were obtained. Obviously, it is the α-substitution which prevents the usual 1,4-reduction to give a nitroalkane and dictates the course of reduction to produce an oxime. The exact role of zinc borohydride for this selectivity is not clear and is under investigation. Whatever be the reasons, zinc borohydride in DME provides a facile and efficient route for the synthesis of ketoximes and nitroalkanes under a

Table-1. **Reduction of conjugated nitroalkenes with zinc borohydride in DME**

			product (% yield)[a]	
entry	conjugated nitroalkene	time(h)	oxime[b]	nitroalkane
1	1-nitrocyclopentene	0.75	75	-
2	1-nitrocyclohexene	1	90	-
3	1-nitrocycloheptene	1.5	91	-
4	$Ph\text{-}CH{=}C(Me)NO_2$	6	81	-
5	$Ph\text{-}CH{=}CH\text{-}NO_2$	6	-	88
6		7	80	-
7		6	-	93
8		6	73	-
9		12	-	88
10		7	82	-
11		6	-	88
12		6	-	90
13		10	-	86
14		6	-	93

---

[a] Yield of isolated pure products, fully characterized by their IR, NMR data

[b] mixture of E and Z isomers.

mild condition. Moreover, zinc borohydride is neutral and can tolerate a number of sensitive functional groups like, carboxylic ester, nitro, halogen substituents on aromatic nuclei, ketal and nitrile.[6] These advantages make this procedure useful for selective reduction of nitroalkene in polyfunctional molecules.

In conclusion, the reduction of conjugated nitroalkenes with zinc borohydride in DME under the present condition producing nitroalkanes or oximes based on the absence or presence of α-substitution in nitroalkenes is interesting and being explored further. Morever, this methodology provides a useful and attractive route for the synthesis of nitroalkenes and oximes.

Acknowledgement. Financial assistance from DST, New Delhi (Grant No. SP/S1/G-49/88) is gratefully acknowledged. R.C. thanks C.S.I.R. for his fellowship.

References and Notes.

1. Barrett, A.G.M. (ed.) 'Nitroalkanes and Nitroalkenes in Synthesis', Tetrahedron Symposia-in-Print, Tetrahedron **1990**, 46, 7313-7598.

2. Hudlicky, M. 'Reductions in Organic Chemistry', Ellis Horwood Limited : Chichester, England, 1984.

3. Kabalka, G.W.; Guindi, L.H.M.; Varma, R.S. Tetrahedron **1990**, 46, 7443.

4. (a) Gilsdorf, R.T.; Nord, F.F. J. Am. Chem. Soc. **1952**, 74, 1837.

   (b) Mourad, M.S.; Varma, R.S.; Kabalka, G.W. J. Org. Chem. **1985**, 50, 133.

5. (a) Shechter, H.; Ley, D.E.; Robertson, Jr. E.B. J. Am. Chem. Soc. **1956**, 78, 4984.

   (b) Meyers, A.I.; Sircar, J.C. J. Org. Chem. **1967**, 32, 4134.

6. (a) Sarkar, D.C.; Das, A.R.; Ranu, B.C. J. Org. Chem. **1990**, 55, 5799.

   (b) Ranu, B.C.; Das, A.R. J. Chem. Soc. Chem. Commun. **1990**, 1334.

(c) Ranu, B.C.; Chakraborty, R. Tetrahedron Lett. **1990**, 31, 7663.

(d) Ranu, B.C.; Das, A.R. J. Org. Chem. In press.

(e) Ranu, B.C.; Basu, M.K.; Tetrahedron Lett. In press.

7. Crabbe, P.; Garcia, G.A.; Rius, C. J. Chem. Soc. Perkin Trans.1 **1973**, 810.

8. Nitroalkenes were prepared according to the procedures :

(a) Corey, E.J.; Estreicher, H. J. Am. Chem. Soc. **1978**, 100, 6294.

(b) Gairaud, C.B.; Lappin, G.R. J. Org. Chem. **1953**, 18, 1.

9. To check the preparative utility, the reaction has been scaled up in multigram quantities in few cases.

10. The reduction of a few α-substituted nitroalkenes (entries 4,6,8,10) being very slow at 0-5°C, were carried out at room temperature.

(Received in UK 17 April 1991)