Zeolite (H-ZSM 5)-catalysed reduction of conjugated nitroalkenes with sodium cyanoborohydride[1]

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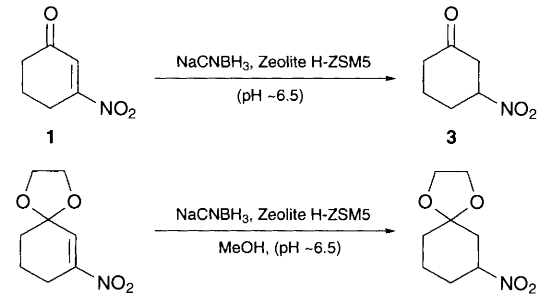
Conjugated nitroalkenes are readily reduced to the corresponding nitroalkanes with sodium cyanoborohydride in the presence of the zeolite H-ZSM 5 in methanol.

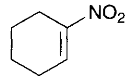
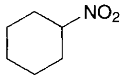
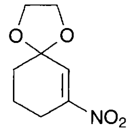
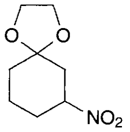
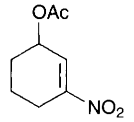
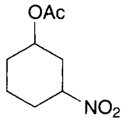
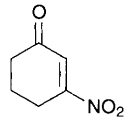
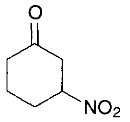
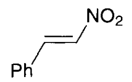
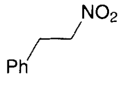
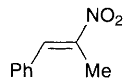
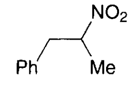
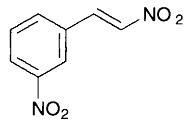
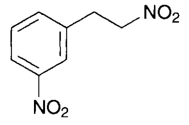
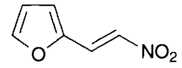
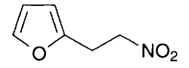
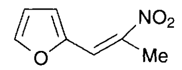
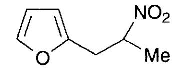
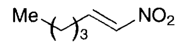
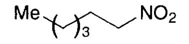
The chemistry of aliphatic nitro compounds has been very useful in contemporary organic synthesis.[2] The importance of aliphatic nitro compounds mainly stems from the versatility of the nitro group. For example, the primary and secondary nitro group can be readily transformed into yet another versatile functionality *viz.* a carbonyl group *via* the well known Nef reaction.[3] Easy deprotonation α to a carbonyl or a secondary nitro group allows[4] C–C bond formation readily. Subsequently, the nitro group could either be reduced[2a,b,4] to an amino group or replaced[2d,5] by a hydrogen *via* tributyltin hydride-based reductions. Under certain circumstances of functional group dispositions, the nitro group is also known to function as a good leaving group. Thus, for instance, allylic nitro compounds permit[6] ready displacement of the nitro group by a variety of nucleophiles, especially in the presence of a palladium(0) catalyst. In addition to this, α-nitroepoxides have been found[7] to function as α-keto carbocation equivalents by virtue of the nitro group behaving as a good leaving group. More recently, the utility of aliphatic nitro compounds in asymmetric synthesis[8] and in carbohydrate chemistry[2d,9] has also been reported. Besides this, conjugated nitroalkenes have been recognised as excellent Michael acceptors[10,11] and dienophiles in Diels–Alder reactions[12] and many methods for their synthesis have been reported[12a,13] in the literature. The importance of nitroaliphatics (*vide-supra*) and the availability of a number of methods for the synthesis of conjugated nitroalkenes increases scope for converting the later into their saturated analogues. A number of reducing agents[11a,13a,14] such as $NaBH_4$, trialkylborohydrides, 2-phenylbenzimidazole and Hantzsch esters have been reported in the literature. However, some of them suffer from the formation of side products, a major drawback resulting in low yields of the desired nitroalkanes. These side products mainly originate due to the Michael addition of the nitronate intermediates to the nitroalkenes themselves. The formation of such dimeric side products has been reduced by manipulating the choice of solvents and pH of the reaction medium.[15] Likewise careful control of pH of the reaction medium along with the use of $NaCNBH_3$ was also found[16] to give improved yields of the desired nitroalkanes. However, in these cases control of pH was effected by employing concentrated hydrochloric acid. In connection with another project we became interested in reducing the nitro enone **1** and the nitroalkene acetal **2** (Scheme 1) to nitroaliphatics **3** and **4** respectively under these conditions. However, we met with little success as the yields of the desired products were too low. It appeared necessary to perform these reactions under mildly acidic conditions.

Recently,[17] there has been a surge of interest in employing zeolites such as H-ZSM 5, TS 1 and Y zeolites in various organic transformations. These catalysts provide defined pore size, thereby allowing selective reactions with molecules having the correct shape and size. Moreover these catalysts, being heterogenous, provide easy workup of the reactions. Besides, they are non-toxic, non-polluting and can be recycled. The



Scheme 1

Table 1 Reduction of nitroalkenes to nitroalkanes

Entry	Nitroalkenes	Nitroalkanes	*t*/h	Yield (%)
1			1	79
2			1	78
3			2	74
4			2	70
5			1	75
6			3	70
7			1	75
8			6	69
9			3[a]	65
10			2	75

[a] The reaction mixture was heated to 50 °C.

zeolite H-ZSM 5 has recently been found by us[17c] to permit regioselective isomerisation of glycidic esters into α-hydroxy-β,γ-unsaturated esters. In this communication we report that a combination[‡] of $NaCNBH_3$ and zeolite H-ZSM 5 (Si : Al, 35 : 1) readily transforms a variety of conjugated nitroalkenes into the corresponding saturated nitro compounds. This includes reduction of the nitro enone **1** as well as the nitroalkene acetal **2** without affecting the carbonyl group and the acetal moiety. The yields[§] of the reduced products were in the range of 65 to 79%. With the exception of one example (*cf.* Table 1, entry 8), which needed 50 °C for the completion of the reaction, all the other nitroalkenes were reduced at 0 °C to room temperature within 1 to 6 hours. The optimum experimental conditions involved the use of half an equivalent of the zeolite H-ZSM 5 with one equivalent of $NaCNBH_3$ in methanol.[¶] The pH of the reaction medium was found to be *ca.* 6.5. It appears that these reaction conditions permit the nitronate salt to be immediately neutralised by the zeolite before dimerisation occurs. Ethanol as the reaction medium proved to be less effective in terms of yield of the reduced products. We believe that, because of the relatively mild and neutral conditions, this method will be useful in contemporary organic synthesis.

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Footnotes

[†] Undergraduate research participant. Part of this research project is taken from the M.Sc. dissertation entitled 'Developement of Newer Synthetic Methods related to the Chemistry of Conjugated Nitroolefins', submitted by Mr Azizul Haque to the I. I. T. Kanpur India in April 1995.

[‡] The reaction did not take place in the absence of the zeolite H-ZSM 5.

[§] The yields refer to the purified (column chromatography) products. However, no attempts were made to isolate the minor by-products.

[¶] *Typical experimental procedure*: To a solution of a nitroalkene (2 mmol) dissolved in dry methanol (3 ml) was added H-ZSM 5 (0.5 mass equiv.). After stirring this mixture at 0 to 5 °C for a few minutes, a methanolic solution (3 ml) of the $NaCNBH_3$ (2 mmol) was added to it in a dropwise fashion. After 10–15 min of stirring, the ice bath was removed and stirring continued for the time indicated in Table 1. At the end of the reaction (UV monitoring) the reaction mixture was filtered through a pad of Celite and the residue washed with dichloromethane (30 ml). The combined organic layers were dried over anhydrous sodium sulfate and the solvent removed under reduced pressure. Purification of the crude product by column chromatography (SiO_2) gave pure nitroalkanes, which were characterised by spectral and analytical means. All the new compounds gave satisfactory analytical data.

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