A Facile Procedure for the Conversion of Nitroolefins into Carbonyl Compounds Using Al-$NiCl_2$•$6H_2O$-THF System

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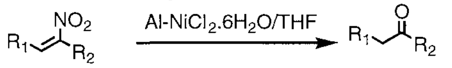
It has been demonstrated that a variety of nitroolefins can be efficiently converted into the corresponding carbonyl compounds by the reaction with an Al-$NiCl_2.6H_2O$-THF system.

The versatility of aliphatic nitro compounds as a precursor to a wide variety of building blocks and intermediates in organic synthesis is an established fact.[1-7] The reduction of conjugated nitroalkenes provides an easy access to a large spectrum of organic functionalities including nitroalkanes,[8] N-substituted hydroxylamines,[9] amines,[10] ketones,[11,12] and oximes.[13,14] Although the transformation of nitroolefins to ketones is an important protocol in organic synthesis, usage of expensive reagents, strong acid and bases, longer reaction time etc. always demands introduction of newer and cheaper reagents which can effect the conversion under very mild reaction condition.

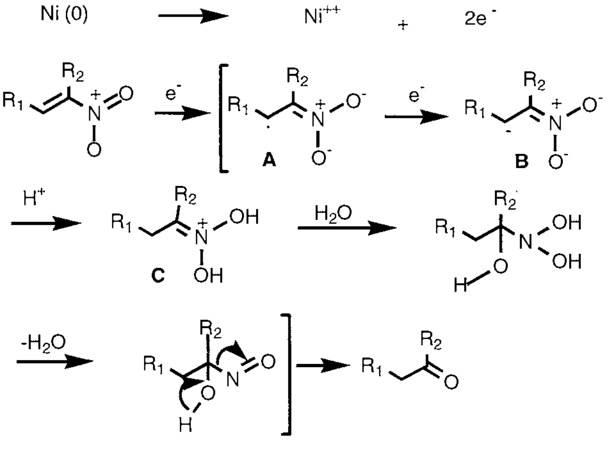
In recent years, more and more report of usage of different metal-metal salt combination for bringing about useful organic transformations are appearing in the literature.[8] In such combinations elementary metal part needs to be more electro-positive than the metal part of the salt.[9] Such combinations which gained importance as reducing systems applicable in organic synthesis are Al-$NiCl_2.6H_2O$,[15] Fe-$NiCl_2.6H_2O$[16] etc. The reducing property exhibited by these metal-metal salt combinations proceed through transfer of one electron from the metal surface (or metal in solution) to the substrate. Another important aspect of these combinations is the Nernst potential difference of M/M^+ viz Cd/Cd^{2+}, Mg/Mg^{2+}, Sn/Sn^{4+} etc. on which activity as well as reactivity of these reagents depend. The mild reducing property of Al-$NiCl_2.6H_2O$ was reported by us for bringing about various organic transformations.[15]

In order to explore the versatility of this reducing system as well as our continued interest on the chemistry of nitroaliphatics,[17] we attempted reduction of nitroolefins to saturated nitroalkanes by Al-$NiCl_2.6H_2O$ in THF. However we observed that the products of the reactions were not the saturated nitroalkanes, instead the corresponding carbonyl compounds were obtained in excellent yield.



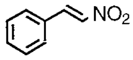
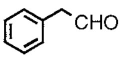
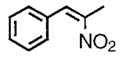
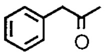
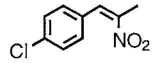
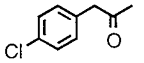
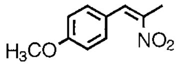
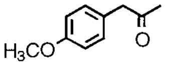
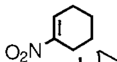
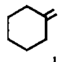
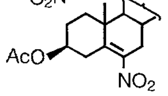
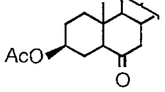
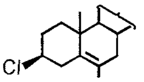
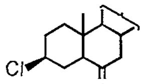
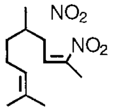
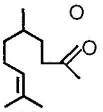
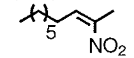
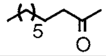
This observation has been generalised through entries 1 to 9 in Table 1.

We believe that reaction with Al-$NiCl_2.6H_2O$ proceeds through a SET process. The nitroalkene being a strong Michael acceptor, traps electrons released during oxidation of Ni(0), produced in the reaction of $NiCl_2.6H_2O$ and aluminium, to Ni^{2+}. The species 'B' picks up protons from HCl generated from hydrolysis of $AlCl_3$ to give 'C' which gets converted to the corresponding carbonyl compound as shown in scheme 1.



Scheme 1.

Table 1. Conversion of nitroolefins into carbonyl compounds

Entry	Nitroolefins[a]	Product[b]	Yield[c] %	MP/BP °C
1			77	195
2			76	216
3			89	gum
4			79	145[d]
5			82	155
6			61	126
7			60	129
8			88	oil
9			88	oil

[a]All the nitroolefins were prepared by following standard literature procedures and characterised by IR, ^1H NMR and MS before performing the reactions. [b]All the carbonyls were characterised by IR, ^1H NMR and MS. [c]Yield refers to that of the pure isolated products. [d]At 25mm of Hg.

To a freshly mixed solid mixture of aluminium powder (2.2mmol) and $NiCl_2.6H_2O$ (4.2mmol) was added a solution of the substrate (0.23mmol) in freshly distilled THF (10 ml). A vigorous exothermic reaction took place which subsided after

20-30 min. When TLC of the reaction mixture showed disappearance of the starting material, the reaction mixture was diluted with THF (100 ml) and filtered. Filtrate was evaporated off and the residue purified by using preparative thin layer chromatotography.

In order to establish the applicability of this transformation at a larger preparative scale, reactions of 1-nitro-2-phenyl ethylene (entry 1) and 1-nitrocyclohexene (entry 5) were performed in 100 mmol scale with this reagent system which gave the corresponding products 2-phenyl acetaldehyde and cyclohexanone respectively in consistent yields.

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References

1 R. Ballini and M. Petrini, *J. Chem. Soc., Perkin Trans. 1*, **1992**, 3159.
2 R. Ballini and G. Bosica, *Synthesis*, **1994**, 723.
3 E. G. Occhiato, A. Guarna, F. D. Sarlo and D. Scarpi, *Tetrahedron: Asymmetry*, **6**, 2971 (1995).
4 M. S. Bezbarua, A. K. Saikia, N. C. Barua, D. Kalita, and A. C. Ghosh, *Synthesis*, **1996**, 1289.
5 R. S. Verma and G. W. Kabalka, *Heterocyles*, **24**, 2645 (1986).
6 G. W. Kabalka and R. S. Verma, *Org. Prep. Proced. Int.*, **19**, 2837 (1987).
7 G. Rosini and R. Ballini, *Synthesis*, **1988**, 833.
8 R. S. Verma and G. W. Kabalka, *Synth. Commun.*, **15**, 151 (1985).
9 M. S. Mourad, R. S. Verma, and G. W. Kabalka, *J. Org. Chem.*, **50**, 133 (1985).
10 M. S. Mourad, R. S. Verma, and G. W. Kabalka, *Synth. Commun.*, **14**, 1099 (1984).
11 M. S. Mourad, R. S. Verma, and G. W. Kabalka, *Synthesis*, **1985**, 654.
12 R. S. Verma, M. Verma, and G. W. Kabalka, *Tetrahedron Lett.*, **26**, 3777 (1985).
13 R. S. Verma, M. Verma, and G. W. Kabalka, *Synth. Commun.*, **16**, 91 (1986).
14 R. S. Verma and G. W. Kabalka, *Chem. Lett.*, **1985**, 243.
15 B. K. Sarma and N. C. Barua, *Tetrahedron*, **47(40)**, 8587 (1991).
16 M. Barua, A. Barua, D. Prajapati, and J. S. Sandhu, *Tetrahedron Lett.*, **37**, 4559 (1996).
17 D. Kalita, A. T. Khan, A. K. Saikia, G. Bez, and N. C. Barua, *Synthesis*, **1998**, 975.