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Tin(II) Chloride Dihydrate Reduction of β,γ-Unsaturated Nitro-alkenes

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Abstract : β,γ-Unsaturated nitro-alkenes have been converted into α,β-unsaturated ketones in good yield by tin(II) chloride dihydrate in tetrahedrofuran.

Conversion of a nitro funtionality into another functional group, most notably the carbonyl group is an important transformation in organic synthesis. Beause of their high nuleophilicity, nitroolefins are valuable precursors to a large number of target molecules as well as important intermediates in organic synthesis especially in carbon--carbon bond formation reactions[1]. Although literature enumerates quite a number of methods for the conversion of a nitro group into a carbonyl group, careful scrutiny of the reaction procedures reveals some shortcoming or other in most of the methods. The Nef reation[2] employs very acidic conditions, others use strong oxidizing[3] or reducing[4] agents likely to affect other functionalities present in the substrate. Some methods use fairly expensive reagents[5]. Moreover, only a very few reagents are mentioned in the literature for the conversion of β,γ-unsaturated nitro compounds to α,β-unsaturated ketones[6]. Herein we describe a method in which this transformation can be affected under mild reaction conditions using Tin(II) chloride dihydrate in tetrahydrofuran.

Condensation of cyclohexanone with nitroethane in the presance of N,N-dimethylethylenediamine furnished 1-nitromethyl cyclohexene <u>1a</u> in quantitative yield[6b]. In a typical procedure a solution of <u>1a</u> (1 mmol) in 4 ml THF was treated with $SnCl_2.2H_2O$ (3 mmol) with stirring at room temperature and the reaction was monitored by TLC. After 6 hours when the starting material had disappeared, the reaction mixture was diluted with 100 ml water and extrated with dichloromethane (3x100 ml). The washed

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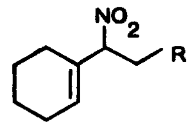

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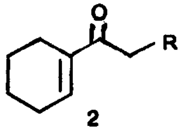

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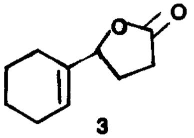


3

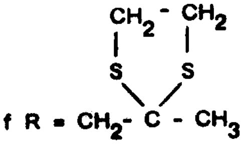
a R = H

b R = OAc

c R = CH_2COCH_3

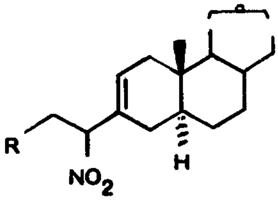
d R = $CH_2CH(OH)CH_3$

e R = $CH_2CH\ (OAc)\ CH_3$



f R = $CH_2\text{-}C\text{-}CH_3$ ($CH_2\text{-}CH_2$, S, S)

g R = CH_2COOMe



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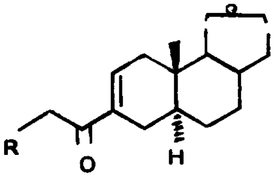

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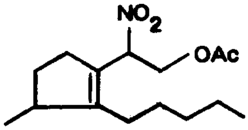
a R = OAc

b R = H



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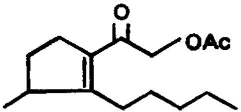

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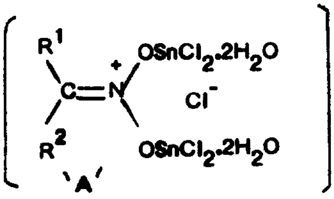
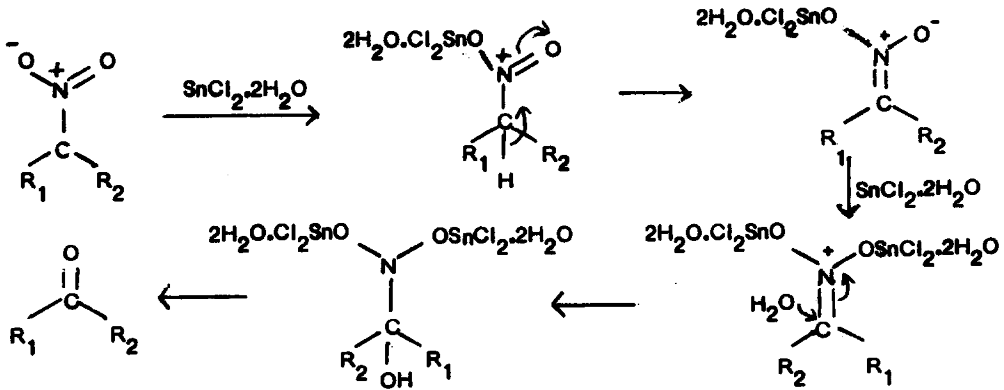


'A'



Scheme

and dried extract was evaporated under reduced pressure to furnish an oil which was purified by preparative TLC to obtain 70% of 2a. Similarly compounds 1b-1f, 4 and 6 gave the corresponding α,β -unsaturated ketones 2b-2f, 5 and 7 respectively in yields as mentioned in the Table 1. Reaction of 1g with $SnCl_2.2H_2O$ gave the lactone 3 as the major product in 60% yield. From the examples cited it becomes apparent that this reagent is very mild and nonsensitive to other functionalities like double bond, carbonyl group, dithioacetal group etc. under these reaction conditions.

The possible mechanism for this transformation can be proposed to be taking place through the hydrolysis[7] of the intermediate stannylnitronate[5] of the type 'A'. Formation of 'A' is possible due to strong co-ordination of Tin(II) chloride with oxygen of the nitro group which facilitates the removal of the proton from the α-carbon atom (Scheme).

This is an example of the striking similarity between silicon and tin reagents as has been recently revealed in several literature reports[8].

Recent publication revealing that tin(II) chloride can be used for efficient cleavage of acetals to carbonyl compounds has prompted us to put our results on record[9].

Table 1[a]

Sl.No.	Entry	Product	Time	Yield[b] (%)
1	1a	2a	6h	80
2	1b	2b	6h	80
3	1c	2c	8h	78
4	1d	2d	8h	75
5	1e	2e	8h	70
6	1f	2f	8h	70
7	1g	3	8h	60
8.	4a[c]	5a	6h	80
9.	4b[c]	5b	6h	80
10	6	7	6h	50

a. All products were characterised by IR, NMR, MS spectral analysis.

b. Isolated yield. A small amount (5-10%) of the hydroxy compounds, formed by the direct displacement of the nitro group, was also isolated in each case except 1g.

c. Compound 4a and 4b belong to cholestane series.

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