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OXIDATIVE CONVERSION OF ALIPHATIC NITROCOMPOUNDS TO CARBONYLS USING SODIUM CHLORITE

Roberto Ballini and Marino Petrini*

Dipartimento di Scienze Chimiche dell'Università
Via S.Agostino,1 I-62032 Camerino Italy

Summary : Aliphatic Nitrocompounds are converted to corresponding Carbonyls by means of Sodium Chlorite under phase transfer catalysis conditions (CH_2Cl_2-NaOH-1N-Bu_4NHSO_4).Primary nitrocompounds give aldehydes while secondary nitroalkanes give ketones in good yields.

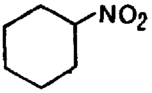
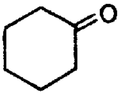
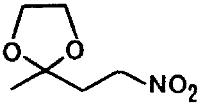
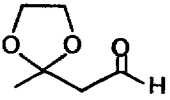
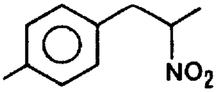
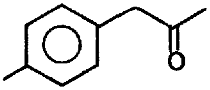
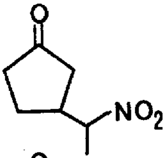
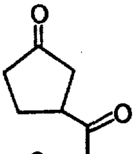
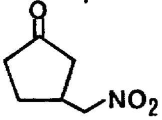
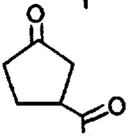
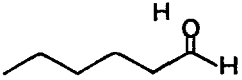
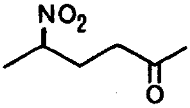
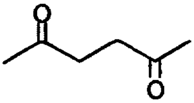
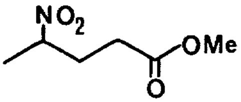
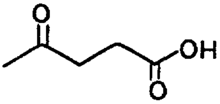
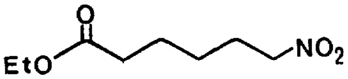
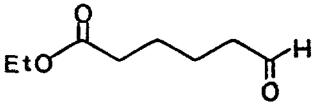
The importance and the role of nitrocompounds in organic synthesis are nowadays well established and have been extensively reviewed [1]. Nitroalkanes are indeed powerful synthetic tools because they facilitate the carbon-carbon bond-forming processes and moreover they can be easily converted into many other useful functionalities. One of the first transformations which involved the nitrogroup was its conversion into carbonyl and since the discovery by Nef in 1894 many methods to accomplish it have been developed[2].

Among them a certain number of systems employs oxidative conditions and operate on the salts of nitroalkanes (Nitronates) which are easily obtained by their treatment with bases. Trialkyl silyl nitronates of secondary nitrocompounds can also be cleaved upon treatment with *m*-chloro perbenzoic acid affording the corresponding ketones in good yields[3]. The most employed oxidant for this conversion is undoubtedly the MnO_4^- ion which has been used under various conditions[4] . Other reagents such as MoOPH[5], t-BuOOH[6], *m*-iodoxybenzoic acid[7] or Singlet Oxygen[8] give satisfactory results with secondary nitroalkanes but produce very low yields of aldehydes or acids when primary nitrocompounds are used.

During recent years our research interests have been focused on increasing synthetic potentialities of aliphatic nitrocompounds in organic synthesis. In this context we have realized a new method to carry out the nitro to carbonyl transformation in a mild and selective fashion. Sodium chlorite has found only limited applications in organic synthesis; it can oxidise aldehydes to acids in acidic conditions but in every case a chlorine scavenger must be used in order to avoid undesired side reactions[9]. To the best of our knowledge no examples of utilizations of this reagent have been reported in non acidic conditions or with other substrates.

Using Sodium Chlorite in a biphasic system (CH_2Cl_2-NaOH 1M) with Bu_4NHSO_4 which acts as phase transfer catalyst we were able to achieve the conversion of nitrocyclohexane into nitrocyclohexanone in 85% yield.
No results were obtained in neutral or acidic conditions (CH_2Cl_2-HCl 1M) and starting material together with some decomposition products have been recovered from reaction mixture. The rate of reaction is dependent upon base concentration; with solutions of NaOH lower than 1M or with 10% K_2CO_3 the conversion of nitroalkane become very slow and a large amount of condensation products are observed on strenghtening the base solution. Hypochlorite ion which makes necessary the use of scavengers like resorcinol or sulfamic acid when sodium chlorite is used in acidic conditions, is not formed in apreciable amount during our process. As a matter of fact, reaction of nitrocyclohexane with 5% NaClO in similar conditions gives 1-chloro-1-nitrocyclohexane as major product while in our reaction, using nitrocyclohexane as substrate, only a small amount of it (4%) is formed.

A typical *experimental procedure* is as follows:
Nitrocompound (5m.mol) is dissolved in CH_2Cl_2 (15 ml) and tetra-*n*-butylammonium hydrogen sulfate (0.5 m.mol) is then added. The solution is cooled by ice bath and then NaOH 1M(15 ml) is poured into the solution followed by solid $NaClO_2$ (80% purity, 0.75 m.mol). After 10 min. the ice bath is removed and stirring is continued at r.t. for the appropriate time (see table). After separation of the two layers the aqueous phase is washed with dichloromethane[10] and then the combined organic phases are washed with brine and dried over $MgSO_4$. Concentration of the solution affords the crude product which can be purified by distillation or chromatographic methods.

ENTRY	SUBSTRATE	PRODUCT[a]	YIELD[b] (%)	REACT. TIME (h)
1			85	8
2			68	0.5
3			65	24
4			80	4
5			67	1
6			70[c]	0.7
7			78	7
8			75	24
9			65	1

a) Satisfactory I.R.,N.M.R. and Elemental analyses were obtained for all compounds.

b) Yelds reported are for isolated pure compounds.

c) Isolated as (2,4 dinitrophenyl)hydrazone derivative m.p. 104°C.

Secondary nitrocompounds are transformed in ketones in good yields; primary nitroalkanes are converted into aldehydes but yields are usually lower[11]. Certain other functionalities e.g. ketal protection or carbonyl groups may also be present in the substrates and are not affected by the reaction conditions but longer reaction times (entry 8) may cause hydrolysis of base sensitive groups.

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References and Notes

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2- For a list of various methods see ref. 1b note 51

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10-In case of entry 8 in which acid is formed the basic aqueous solution is acidified with NH_2SO_3H before extracting with CH_2Cl_2

11-Less clean reaction mixtures are observed when primary nitroalkanes are used. A small amount of the corresponding acid (5%) is often isolated.

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