

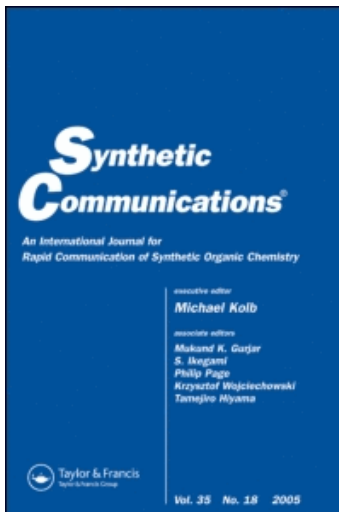
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Synthetic Communications

Publication details, including instructions for authors and subscription information:

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To cite this Article Vankar, Padma S. , Rathore, R. and Chandrasekaran, S.(1987) 'A Mild and Selective Method for the Conversion of Nitroalkanes to Carbonyl Compounds', *Synthetic Communications*, 17: 2, 195 – 201

To link to this Article: DOI: 10.1080/00397918708057221

URL: <http://dx.doi.org/10.1080/00397918708057221>

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A MILD AND SELECTIVE METHOD FOR THE CONVERSION
OF NITROALKANES TO CARBONYL COMPOUNDS

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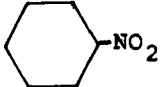
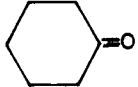
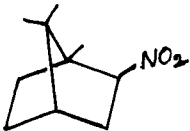
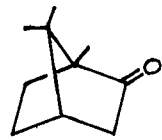
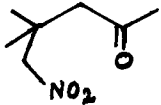
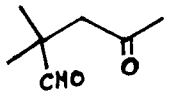
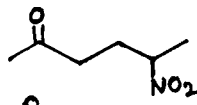
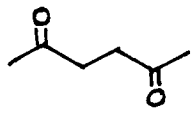
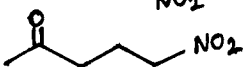
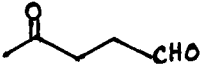
Nef reaction is one of the most commonly used method for the conversion of nitroalkanes to carbonyl compounds. It was found that the salt of primary nitroparaffins are transformed into aldehydes and those of secondary nitro compounds into ketones, when they are treated with aqueous acid.¹ A number of modifications and alternate procedures for effecting this transformation have been reported.² In fact most of the modified procedures appeared in the literature after the work of Schecter and Williams^{2a} using potassium permanganate as the oxidant. Recently, Kornblum³ and Steliou⁴ reported useful modifications of the original permanganate procedure.^{2a} Although the yield of the carbonyl compounds

is generally high in simple nitroalkanes using the modified permanganate procedures,^{3,4} the yield drops down considerably in the case of substrates containing other oxidizable functional groups like carbon-carbon double bonds and hydroxyl groups. Hence a need still exists for the development of a methodology which is mild and more selective.

In the course of our oxidation studies with cetyltrimethylammonium permanganate^{5a} we find that this stable quarternary ammonium permanganate (CTAP) oxidises benzylic alcohols selectively^{5b} and cleaves carbon-nitrogen double bonds with ease.^{5c} These studies have now been extended to the conversion of nitroalkanes to carbonyl compounds and herein we report our results in this area. The method, which seems to be general, simply involves the reaction of nitroalkane with triethylamine in dichloromethane at room temperature to generate the nitronate anion which when reacted with 1.5 equivalents of freshly prepared cetyltrimethylammonium permanganate^{5a} for 3-5 h afford the corresponding carbonyl compounds in good yield.

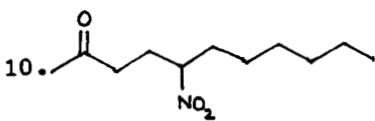
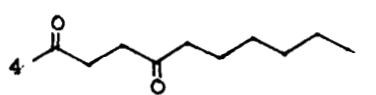
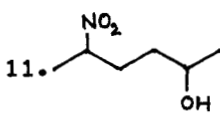
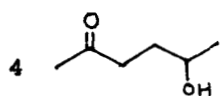
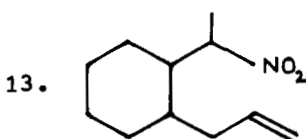
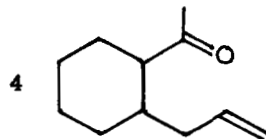
The scope of the methodology can be gauged from the wide range of substrates entered in the Table. Note that in all cases yields of isolated products are good and that conditions are mild. It is important to note the generation of 1,4-dicarbonyl compounds (entries 7-

TABLE

Entry	Substrate	Time (h)	Product ^a	Yield ^b (%)
1.	Ph-CH ₂ -NO ₂	3	Ph-CHO	89
2.	Ph-CH ₂ -CH ₂ -NO ₂	3.5	Ph-CH ₂ -CHO	80
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Ph}-\text{CH}-\text{NO}_2 \end{array}$	3	$\begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{C}-\text{CH}_3 \end{array}$	87
4.	CH ₃ (CH ₂) ₅ -CH ₂ -NO ₂	3	CH ₃ (CH ₂) ₅ -CHO	71
5.		4		80
6.		5		65
7.		5.5		62
8.		4		65
9.		4		57

....contd.

Table (contd.)

Entry	Substrate	Time (h)	Product ^a	Yield ^b (%)
10.		4		64
11.		4		62
12.	$\text{CH}_2=\text{CH}(\text{CH}_2)_8-\text{CH}_2\text{NO}_2$	3.5	$\text{CH}_2=\text{CH}(\text{CH}_2)_8-\text{CHO}$	66
13.		4		67

a. Products were characterised by comparison with authentic samples (spectra, TLC, m.p. and m.p. of 2,4-dinitrophenylhydrazone.

b. All yields refer to isolated products.

10) and the isolation of aldehydes (entries 1, 2, 4, 7) without overoxidation to carboxylic acids. The mildness and selectivity of the reagent is exemplified in the reaction of nitroalcohol (entry 11) where the carbonyl compound is obtained in the presence of an easily oxidizable secondary hydroxyl group. Especially significant selectivity is observed in the reaction of olefinic nitro compounds (entries 12 and 13) where the products are obtained in better yields without attack at the carbon-carbon double bond.

Although many methods are well known^{1,2} and continue to be developed^{3,4} for the conversion of nitro to carbonyl group our procedure offers mildness and selectivity; Cetyltrimethylammonium permanganate (CTAP) is relatively more stable than some of the other quaternary ammonium permanganates and is easy to handle.

General Procedure : To a stirred solution of nitro compound (2 mmol) in dichloromethane (15 ml) is added triethylamine (2 mmol) in dichloromethane (2 ml) dropwise. After stirring for 10 min., a solution of CTAP (3 mmol) in dichloromethane (5 ml) is added over a period of five minutes. Stirring is continued for 3-5 h and the reaction mixture is concentrated to half its volume under reduced pressure. The residual solution is diluted with ether (50 ml) and filtered through a pad of Celite and anhydrous magnesium sulphate. The filtrate

is evaporated under reduced pressure and the residue is purified by flash chromatography to reveal the carbonyl compound.

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