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A Novel One Pot Synthesis of α-Nitroketones from Olefins using Trimethylsilylnitrate-Chromium Trioxide Reagent System[1]

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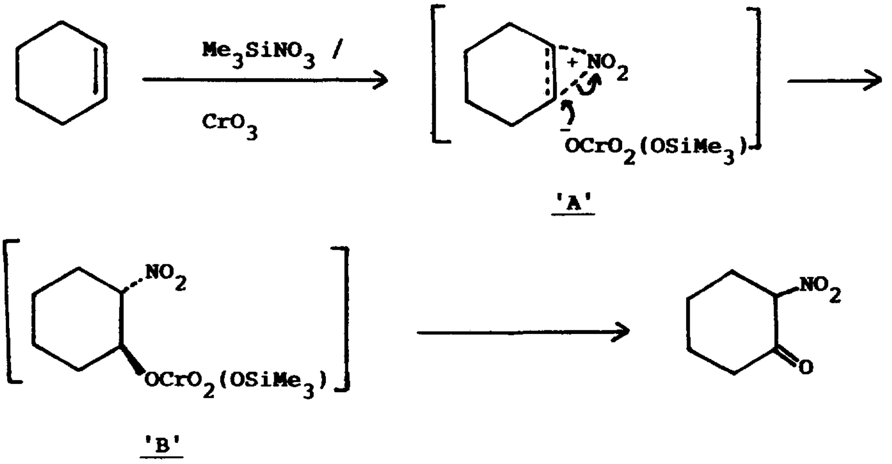
Abstract: *A variety of α-nitroketones have been obtained from the corresponding olefins in good yields upon reaction with trimethylsilylnitrate-chromium trioxide reagent system.*

α-Nitroketones are useful intermediates in organic synthesis[2,3]. In recent years their utility in the synthesis of a variety of important structural units has been well explored[4]. As a result of this, several approaches towards their preparation have been reported in the literature[4,5]. Some of the most commonly employed methods towards cyclic α-nitroketones involve treatment of an enol acetate, a potassium enolate or an enol silyl ether with nitric acid[6], pentyl nitrate[7] or nitronium tetrafluoroborate[8] respectively. More recently[9] reaction of an enol acetate with trifluoroacetic anhydride and ammonium nitrate has been found to be a better alternative over nitric acid in terms of improved yields and mild reaction conditions. During their studies related to electron transfer processes Kochi et al[10] have found that tetranitromethane reacts readily with enol silyl ethers to yield the corresponding α-nitroketones. Cyclic olefins are also known[11] to give the corresponding α-nitroketones directly when reacted with dinitrogen tetroxide in the presence of oxygen. On the other hand acyclic α-nitroketones are generally prepared by oxidation[12] of the corresponding 2-nitroalkanols and by C-acylation[13] of nitroalkanes.

Although the above described methods towards cyclic and acyclic α-nitroketones are being followed, there appears to be a need to develop newer methods for their synthesis particularly from olefins as they are the simplest starting materials for α-nitroketones. Towards this effect it appears that one of the most plausible ways is to react olefins with a nitronium ion source followed by a nucleophilic oxidising agent.

In this communication we wish to report that a combination of trimethylsilylnitrate (prepared *in situ* from silver nitrate and chlorotrimethylsilane[14]) and chromium trioxide readily converts cyclic as well as acyclic olefins into the corresponding α-nitroketones in good yields (cf. Table 1) with the exception of α-nitrocyclopentanone[15] which is obtained in 27% yields only. The reaction is fairly clean and proceeds under mild (0^0 C to ambient temperatures) conditions. We presume that a species such as $O_2N\text{-}O\text{-}CrO_2\text{-}(OSiMe_3)$ is generated *in situ* which acts as a source of $^+NO_2$ and $^-OCrO_2\text{-}(OSiMe_3)$ and eventually reacts with olefins to yield α-nitroketones (cf. Scheme 1). The intermediate 'A' is attacked by the species $^{-}OCrO_2$-($OSiMe_3$) to give another intermediate 'B' followed by the cleavage of the O-Cr bond with concommitant oxidation to yield an α- nitroketone. In case of unsymmetrical olefins the attack of the species $^{-}OCrO_2$-($OSiMe_3$) appears to be governed by the stability of the transient carbocationic intermediate. This allows formation of only one of the regioisomers and only this isomer could be isolated from the reaction mixture.

Judging from the simplicity of this one pot procedure for the synthesis of α-nitroketones in good yields, we believe that it will find application in organic synthesis. To the best of our knowledge this combination of trimethylsilylnitrate and chromium trioxide has not been reported earlier in the literature and we are currently exploring the potential of this reagent system in other organic transformations.



Scheme 1

A general experimental procedure is as follows: To a stirred solution of $ClSiMe_3$ (110 mg, 1 mmol) in 2 ml of dry CH_3CN (if the olefin was not completely miscible with CH_3CN, 0.5 ml of dichloromethane was added to increase its solubility) under nitrogen atmosphere in dark at 0^0 C was added silver nitrate (187 mg, 1.1 mmol) and the mixture was stirred for 1 hr. The resulting acetonitrile solution of Me_3SiNO_3 was separated from the precipitated AgCl by decantation and added to a stirred mixture of chromium trioxide (150 mg, 1.5 mmol) in 1 ml of CH_3CN. After 15 min., an olefin (1 mmol) dissolved in 1 ml of CH_3CN was added very slowly to this reaction mixture (fast addition led to exothermic and vigorous reaction) with occasional cooling with cold water. After the addition was complete, the reaction mixture was stirred for the time indicated in the Table 1. Addition of water followed by usual work up with ether gave almost pure α-nitroketones. These were further purified by column chromatography (silica gel).

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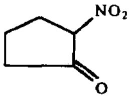
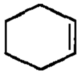
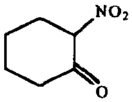
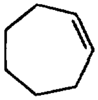
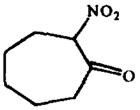
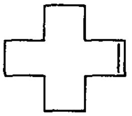
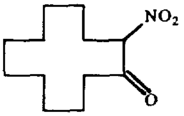
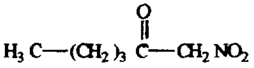
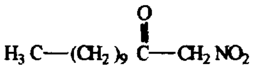
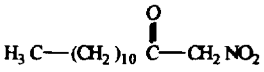
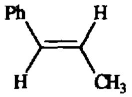
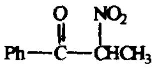
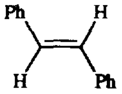
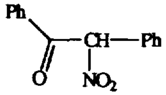
Table 1

Conversion of Olefins into α-Nitroketones

Entry	Olefin	α-Nitroketone	Time (hr)	Yield (%)
1.			24	27
2.			24	61
3.			24	70
4.			24	72
5.	$H_3C—(CH_2)_3CH=CH_2$	 $H_3C—(CH_2)_3\overset{O}{\overset{\|}{C}}—CH_2NO_2$	24	88
6.	$H_3C—(CH_2)_9CH=CH_2$	 $H_3C—(CH_2)_9\overset{O}{\overset{\|}{C}}—CH_2NO_2$	20	94
7.	$H_3C—(CH_2)_{10}CH=CH_2$	 $H_3C—(CH_2)_{10}\overset{O}{\overset{\|}{C}}—CH_2NO_2$	20	81
8.			10	76
9.			10	79*

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* A small amount (7%) of benzaldehyde was isolated in this case which must have resulted due to the C-C bond cleavage.

References and Notes:

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15. It is known in the literature (please see Feuer, H. and Pivawer, P. M. *J. Org .Chem.,* **1966,** *31,* 3152 and also reference number 9 above) that α-nitrocyclopentanone is prone to undergo ring cleavage under different reaction conditions and hence it is therefore not surprising that in the present study we have less yield of this compound.

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