

0040-4039(95)00839-X

A Novel One Pot Nitroacetamidation of Olefins using Ceric Ammonium Nitrate-Sodium Nitrite-Acetonitrile Reagent System¹

M.Venkat Ram Reddy, Bharat Mehrotra² and Yashwant D. Vankar Department of Chemistry, Indian Institute of Technology, Kanpur-208016, INDIA

Abstract: Olefins react with a reagent system comprising of ceric ammonium nitrate - sodium nitrite and acetonitrile to yield products of nitroacetamidation in fair to good yields. Benzonitrile and acrylonitrile have also been found to react with cyclohezene to yield analogous nitroamides.

The chemistry of aliphatic nitro compounds has gained importance³ during the last one and a half decades since the publication of an important review by Seebach⁴. The transformation of a primary and a secondary nitro group into another versatile functionality viz.a carbonyl group, via the well known Nef reaction⁵ has been well utilised in organic synthesis. In addition to this, nitro compounds can also be easily transformed into other useful functionalities such as amines, oximes, nitrile oxides, nitriles etc⁴. Deprotonation ' α ' to the nitro group followed by C-C bond formation is also very useful⁶ in organic synthesis especially when reductive denitration with n-Bu₃SnH is easily possible^{7,8}. On the other hand, tertiary nitro compounds undergo⁸ both inter as well as intramolecular C-C bond formations when treated with n-Bu₃SnH/AIBN via radical pathways. These reactions have also found utility in carbohydrate chemistry⁸. Owing to these important developments and many others^{4,8-11} efforts to discover¹² new methodologies to introduce nitro groups along with other functionalities on readily available substrates have gained momentum.

In this letter we wish to report¹³ that NaNO₂ - ceric ammonium nitrate (CAN)-acetonitrile reagent system reacts with a variety of olefins to produce the corresponding products of nitroacetamidation¹⁴ where the nitro and the *N*-acetyl moieties are vicinally disposed (cf.Table 1). The only exceptions are with styrene and cinnamyl acetate which yielded β -nitrostyrene and β -acetoxymethyl- β -nitrostyrene respectively. Although ceric ammonium nitrate alone also leads to these products, the yields are low and the reactions proceed slowly. While this work was at its final stages a combination of CAN and NaNO₂ in acetic acid was reported by Hwu et al¹² for converting olefins into α , β -unsaturated nitroalkenes. We also believe that species such as [NO₂]^{*} are generated by CAN under the reaction conditions which then adds on to the olefins to form carbon radicals. These radical intermediates are then converted into the corresponding carbocations by CAN which get trapped by CH_3CN eventually leading to the formation of nitroacetamides in a manner analogous to the Ritter reaction¹⁵ (Scheme 1). If the carbocation so formed, loses a proton, instead of being trapped by acetonitrile, the corresponding nitroolefin is formed. This specially appears to be the case where the carbocation is well stabilised (cf.entries 6 and 7) and the proton to be lost is very acidic.





Scheme 1

The lack of stereochemical preference in these reactions or involvement of neighbouring group participation through an acetyl moiety (cf.entry 5) strongly supports the intermediacy of a carbocation. Further, reactions of cyclohexene with benzonitrile and acrylonitrile in place of CH_3CN also gave the corresponding nitroamides (cf. entries 7 and 8) which confirms the generality of this reaction.

In conclusion, we believe that this one pot nitroacetamidation is a useful reaction since it introduces two important functional groups in one step using simple conditions and readily available reagents.

A typical experimental procedure is as follows: To a stirred solution of an olefin (1 mmol) in 5 ml of CH_3CN was added NaNO₂ (5 mmol) and CAN (2 mmol). The reaction mixture was then stirred at room temperature for the time indicated in the Table 1. It was then quenched with a saturated solution of NaHCO₃ and extracted with ethyl acetate. The organic layer was washed with water and then with brine followed by drying over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure yielded crude nitro acetamides. Purification by column chromatography (silica gel) yielded the pure product.

Entry	Olefin	Product	Time (hr)	Yield(%)
	n ⁽	n ⁽ , NO ₂ NHCOCH ₃		
1	n = 1	n=1	24	64
2	n=2	n=2	24	58
3	n=3	n=3	24	71
4	Ph	Ph NHCOCH3	10	35
5	∕_OAc		10	21
6	Ph	Ph NO ₂	5	88
7	Ph 04		10	81
8	(i)	NO ₂ NO ₂ NHCOPh	24	68
9	(iii)	NO2 NHCOCH	24 =CH ₂	71

Table 1: One Pot Nitroacetamidation of Olefins Using Ceric Ammonium Nitrate-CH₃CN Reagent System.

(i) Benzonitrile (2 mmol) per 1 mmol of cyclohexene.

(ii) Acrylonitrile was used as solvent in this case.

References and Notes:

- 1. Part 6 in the series "Chemistry of nitro compounds". For part 5 please see Y.D.Vankar, K.Shah, A.Bawa and S.P.Singh, *Tetrahedron*, 1991, 47, 8883.
- 2. Undergraduate research participant.
- 3. J.Mulzer, H.-J.Altenbach, M.Braun, K.Krohn and H.-U.Reissig, Organic synthesis highlights, VCH, Weinheim, 1991, p.25.
- 4. D.Seebach, E.W.Colvin, F.Lehr and W.Teller, Chimia, 1979, 33, 1.
- 5. R.C.Larock, Comprehensive Organic Transformations, pp 603, VCH Publishers Inc., New York, 1989.
- (i) N.Ono and A.Kaji, Synthesis, 1986, 693. (ii) H.M.R.Hoffmann, Angewandte Chemie, Int. Ed. Engl., 1992, 31, 1332.
- (i) R.Tamura, A.Kamimura and N.Ono, Synthesis, 1991, 423. (ii) Y.-J.Chen and W.-Y.Lin, Tetrahedron Lett., 1992, 33, 1749.
- H.Feuer and A.T.Nielsen, Nitro Compounds, VCH Verlagsgesellschaft mbH, Weinheim, Germany, 1990.
- 9. A.G.M.Barrett and G.G.Graboski, Chemical Reviews, 1986, 86, 751.
- 10. G.W.Kabalka and R.S.Verma, Org. Prep. Proc. Int., 1987, 19, 283.
- 11. G.Rosini, R.Ballini, M.Petrini, E.Marotta and P.Righi, Org. Prep. Proc. Int., 1990, 22, 6707.
- 12. J.R.Hwu, K.-L.Chen and S.Ananthan, J.C.S.Chem.Comm., 1994, 1425.
- 13. This work is partly abstracted from the M.Sc. Dissertation entitled *Chemistry of nitro compounds:* Studies towards the synthesis of some useful nitro compounds submitted by Mr. Bharat Mehrotra to IIT Kanpur,India in April 1994.
- (i) For analogous nitroacetamidation using nitronium tetrafluoroborate and CH₃CN please see M.L.Schienbaum and M.Dines, J.Org.Chem., 1971, 36, 3641 and A.J.Bloom, M.Fleischman and J.M.Mellor, J.Chem.Soc., Perkin Trans I, 1984, 2357. (ii) For electrochemical nitroacetamidation please see A.J.Bloom, M.Fleischman and J.M.Mellor, J.Chem.Soc., Perkin Trans.I, 1986, 79 and idem, Electrochimica Acta, 1987, 32, 785.
- (i) J.J.Ritter and P.P.Minieri, J.Am. Chem.Soc. 1948, 70, 4045. (ii) L.I.Kriemen and D.J.Cota, Org.React. 1969, 17, 213. (iii) D.K.Thakur and Y.D.Vankar, Synthesis, 1983, 223 (iv) Y.D.Vankar and C.T.Rao, Tetrahedron, 1985, 41, 3405. (v) Y.D.Vankar, G.Kumaravel and C.T.Rao, Synthetic Commun., 1989, 2181. and references cited therein.

(Received in UK 23 March 1995; revised 9 May 1995; accepted 12 May 1995)