

CHROMIUM(II) CHLORIDE REDUCTION OF α,β -UNSATURATED NITROALKENES.
A FACILE ROUTE TO CARBONYL COMPOUNDS.

Rajender S. Varma, Manju Varma and George W. Kabalka*

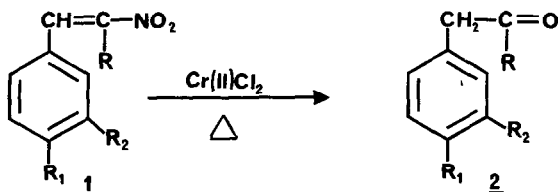
Department of Chemistry, University of Tennessee
Knoxville, TN 37996-1600

Abstract: α,β -Unsaturated nitroalkenes are readily reduced by chromium(II) chloride to the corresponding carbonyl compounds in good yields.

In continuation of our studies on the reduction of conjugated nitroalkenes to useful synthetic precursors such as nitroalkanes,¹ N-substituted hydroxylamines,² amines,³ ketones,⁴ chromenes,⁵ α -alkoxy and α -alkylthio oximes,⁶ and ketones,⁷ we became interested in the synthesis of α -hydroxy oximes. An examination of the literature revealed that chromium(II) chloride reduction of steroidal nitroolefins afford α -hydroxy oxime derivatives.⁸ A recent report⁹ on an unusual reduction of 3-nitroflavones to flavonols by chromium(II) chloride also presumably proceeds via an α -hydroxy oxime intermediate. We decided to explore the use of chromium(II) chloride in the reduction of β -nitrostyrene derivatives. However, when the reductions were carried out as described in the literature,⁸⁻¹¹ the main reaction products were the corresponding carbonyl compounds with trace amounts of α -hydroxyketones;¹² no oxime derivatives were detected¹³ in contrast to earlier studies.^{8,11}

Although transformations of nitroparaffins or their salts to carbonyl compounds (the Nef reaction)¹⁴ have been investigated extensively,¹⁵ the readily accessible conjugated nitroalkenes have received little attention.¹⁶⁻¹⁸ The present study may stimulate the use of low-valent transition metal species in the reduction of conjugated nitroalkenes analogous to their applications in the reduction of the corresponding nitroalkanes.^{15c,15d}

The following procedure is representative: chromium(II) chloride [Alfa] (20 mmol, 2.46 g) was placed in a nitrogen-flushed flask equipped with septum inlet and magnetic stirring bar. Aqueous hydrochloric acid (3%, 30 mL) was injected into the flask followed by the slow addition of the β -nitrostyrene derivative (2 mmol, in 20 mL THF) at room temperature. A moderately exothermic reaction ensued. The mixture was refluxed for 4 hrs. and, after cooling, saturated with sodium chloride. The product was extracted into ether (3 x 30 mL) and worked up in the usual manner. The crude carbonyl compound was purified using a silica gel column (ether/petroleum ether). The results are summarized in Table I.



- a R = R₁ = R₂ = H
b R = CH₃; R₁ = R₂ = H
c R = CH₃; R₁ = Br; R₂ = H
d R = CH₃; R₁ = R₂ = OC₂H₅

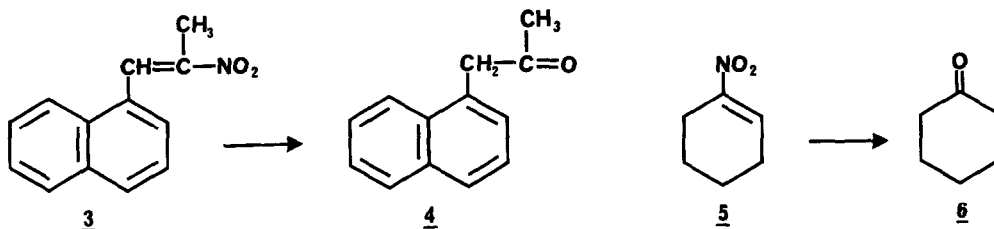


TABLE I. CARBONYL COMPOUNDS FROM NITROALKENES VIA CHROMIUM(II) CHLORIDE REDUCTION

Nitroalkene ^a	Product ^b	Yield ^c [%]	Ref
<u>1a</u>	<u>2a</u>	80	15d
<u>1b</u>	<u>2b</u>	81	4
<u>1c</u>	<u>2c</u>	79	4
<u>1d</u>	<u>2d</u>	78	4
<u>3</u>	<u>4</u>	72	4
<u>5</u>	<u>6</u>	52	13

^aPrepared by the published procedure.² ^bAll products exhibited physical and spectral characteristics in accordance with the assigned structures. ^cIsolated and unoptimized yields.

ACKNOWLEDGEMENT: We wish to thank the Department of Energy for support of this research.

REFERENCES AND NOTES

- R. S. Varma and G. W. Kabalka, *Synth. Commun.*, **14**, 1093 (1984); *Idem, Ibid*, **15**, 151 (1985).
- M. S. Mourad, R. S. Varma and G. W. Kabalka, *J. Org. Chem.*, **50**, 133 (1985).
- M. S. Mourad, R. S. Varma and G. W. Kabalka, *Synth. Commun.*, **14**, 1099 (1984).
- M. S. Mourad, R. S. Varma and G. W. Kabalka, *Synthesis*, 000 (1985).
- R. S. Varma and G. W. Kabalka, *Heterocycles*, **23**, 139 (1985).
- R. S. Varma and G. W. Kabalka, *Chem. Lett.*, 243 (1985).
- R. S. Varma and G. W. Kabalka, *Synth. Commun.*, **15**, 000 (1985).
- J. R. Hanson and E. Premuzic, *Tetrahedron*, **23**, 4105 (1967).
- T. S. Rao, H. H. Mathur and G. K. Trivedi, *Tetrahedron Lett.*, **25**, 5561 (1984).
- A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 1350 (1964).
- S. Ranganathan and B. B. Singh, *J. Chem. Soc. Chem. Commun.*, 218 (1970).
- The reduction of 1-nitrocyclohexene may have produced a significant quantity (~40%) of the corresponding 2-hydroxycyclohexanone. TLC analyses revealed a slower moving spot and a white solid formed on standing. The m.p. range and physical characteristics of the solid are in general agreement with those reported for the dimer of 2-hydroxycyclohexanone (adipoin). [See J. C. Sheehan, R. C. O'Neill and M. A. White, *J. Am. Chem. Soc.*, **72**, 3376 (1950)].
- It has been reported that chromous acetate generates carbonyl compounds from oximes which have been acetylated. [See E. J. Corey and J. E. Richman, *J. Am. Chem. Soc.*, **92**, 5276 (1970)].
- J. U. Nef, *Justus Liebigs Ann. Chem.*, **280**, 264 (1894).
- For leading references see (a) N. Kornblum, A. S. Erickson, W. J. Kelly and B. Henggeler, *J. Org. Chem.*, **47**, 4534 (1982); (b) D. Seebach, E. W. Colvin, F. Lehr and T. Weller, *Chimia*, **33**, 1 (1979); (c) T.-L. Ho, *Synthesis*, 1 (1979); (d) J. E. McMurry, *Acc. Chem. Res.*, **7**, 281 (1974); W. E. Noland, *Chem. Rev.*, **55**, 137 (1955) and references cited therein.
- R. T. Gilsdorf and F. F. Nord, *J. Am. Chem. Soc.*, **74**, 1837 (1952).
- A. B. B. Ferreira and K. Salisbury, *J. Chem. Soc., Perkin Trans. II*, 995 (1978).
- H. B. Hass, A. G. Susie and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950).

(Received in USA 28 May 1985)