Stannous chloride reduction of nitroalkenes to oximes in acetone

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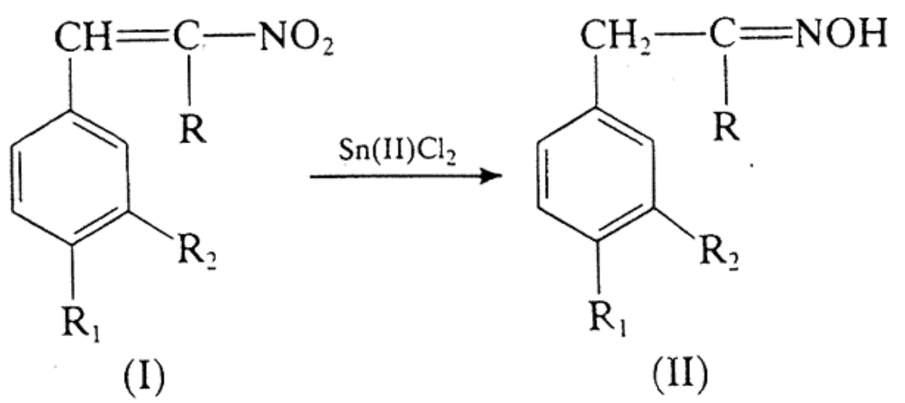
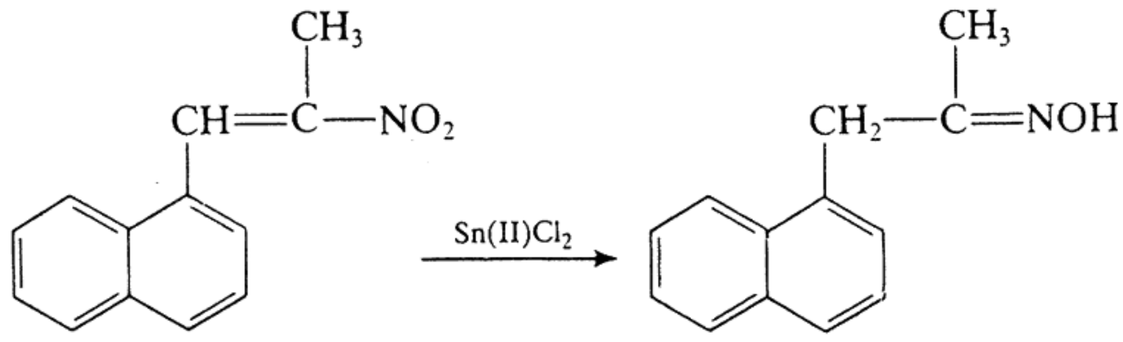
The authors have been investigating the potential utility of nitroalkenes as precursors to a variety of useful synthetic intermediates such as nitroalkanes, *N*-substituted hydroxylamines,[2] amines,[3] ketones,[4] chromenes,[5] α-substituted oximes[6] and ketones.[7] Prompted by a recent report[8] on the use of stannous chloride as a reducing agent in non-acidic and non-aqueous media for conversion of nitroarenes into amines, the authors applied the methodology to reduction of nitroalkenes. Now, it is reported that stannous chloride readily reduces the $\alpha\beta$-unsaturated nitroalkenes to the corresponding oximes in acetone at room temperature (see Table). This appears to be the only instance of oxime formation to appear in otherwise extensive literature on the use of stannous chloride as a reducing agent.[9]



(I) (II)

(*a*) R=R$_1$=R$_2$=H
(*b*) R=Me; R$_1$=R$_2$=H
(*c*) R=Me; R$_1$=Br; R$_2$=H
(*d*) R=Me; R$_1$=R$_2$=OEt



(III) (IV)

General experimental procedure – β-Methyl-β-nitrostyrene (0.65g) and stannous chloride (2.3g) were stirred together in an Erlenmeyer flask at room temperature in acetone. The reaction mixture was poured on to crushed ice, adjusted to pH 8 with aqueous sodium hydrogen carbonate, stirred for 15 min and saturated with sodium chloride. The product was extracted into ether (6 x 30 cm^3), dried ($MgSO_4$), and solvent was removed under reduced pressure. The crude product on column chromatography (silica gel; ether: petroleum, 1:9) gave phenylpropan-2-one oxime (0.44g, 74 per cent) as a thick oil.[10]

Table

Nitroalkene	Yield[a] of oxime[b] (per cent)	Time (min)	Lit. Ref.
(I*a*)	(II*a*) (46)	50	10
(I*b*)	(II*b*) (74)	45	11
(I*c*)	(II*c*) (69)	60	12
(I*d*)	(II*d*) (70)	70	12
(III)	(IV) (71)	60	13

[a] Isolated and non-optimised yield; [b] all oximes were characterised by their physical and spectral (^{1}H-n.m.r., and ^{13}C-n.m.r.) properties and elemental analyses; 2.5 mol eq. of stannous chloride was used except for reduction of (I*d*) where 6 mol eq. were used. All products are thick oils except compound (II*c*) (colourless needles, mp 90-1°C)

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