A FACILE ALDOXIME PREPARATION VIA THE REDUCTION OF α,β-UNSATURATED NITROALKENES USING TIN(II) CHLORIDE

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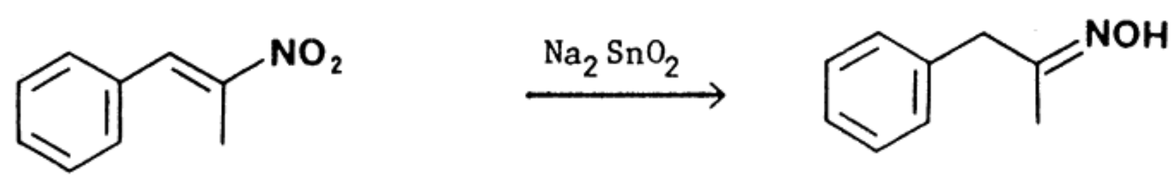
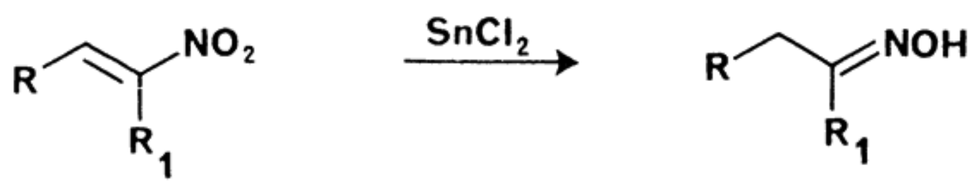
Abstract: α,β-Unsaturated nitroalkenes are readily reduced by $SnCl_2 \cdot 2H_2O$ in ethyl acetate to the aldoximes in high yield at room temperature.

Tin(II) halides have proven to be effective reducing agents in organic synthesis.[1] Reactions involving stannous ions may be carried out under acidic, neutral, or basic conditions and the products obtained are often pH dependent. In an earlier report, we noted that conjugated nitroalkenes were efficiently reduced to the corresponding ketoximes by tin(II) under basic conditions.[2] Unfortunately, the method is not suitable for the preparation of aldoximes due to competing side reactions. A subsequent investigation revealed that ketoximes could also be



generated by carrying out the reactions in neutral solvents.[3,4] Once again, the reaction on conditions were not appropriate for preparationof aldoximes.

We now wish to report that nitroalkenes are readily reduced by $SnCl_2 \cdot 2H_2O$ to the corresponding aldoximes in ethyl acetate at room temperature. Ketoximes are also obtained in excellent yields. The mildness of this method and the purity of the products obtained serve to extend the synthetic utility of stannous chloride, a safe and inexpensive reagent. The results are summarized in Table I.



a. R = n-hexyl R_1 = H
b. R = phenyl R_1 = H
c. R = p-isopropylphenyl R_1 = H
d. R = 1-napthyl R_1 = H
e. R = 9-anthracenyl R_1 = H
f. R = p-bromophenyl R_1 = CH_3
g. R,R_1 = cyclohexyl ring

EXPERIMENTAL

Commercially available samples (Aldrich) of 1-nitro-1-cyclohexene, β-nitrostyrene, and 9-(ω-nitrovinyl)anthracene were used as received. Other nitro compounds were prepared via published procedures.[5] The products were characterized by their physical properties and spectral characteristics (^{1}H-NMR, ^{13}C-NMR etc.).

TABLE I. REDUCTION OF NITROALKENES TO OXIMES WITH TIN(II) CHLORIDE

Product[a]	Time (hr)	yield[b] (%)	H-NMR ($CDCl_3$, δ ppm)				^{13}C-NMR ($CDCl_3$ δ ppm)				Lit. Ref.
			CH/H_3 (Z)	(E)	CH_2 (Z)	(E)	C=NOH (Z)	(E)	CH_2 (Z)	(E)	
2a	4	91	6.65	br	2.18	br	150.3	150.8	---		6
2b	6	94	7.51	6.86	3.74	3.52	150.5	150.6	31.7	35.8	7,8,9
2c	6	92	7.48	6.78	3.71	3.48	150.6	150.8	31.4	35.5	10
2d	8	93	7.63	6.72	4.25	3.96	150.6	150.6	29.7	33.5	11
2e	8	90	7.53	6.76	4.72	4.55	147.8	148.0	24.2	28.0	--
2f	5	89	1.78	1.78	3.62	3.37	157.2	158.1	34.2	41.8	12
2g	2	92	-		-		160.5		-		13

a - Product exhibited physical and spectral properties in accord with the assigned structures.
b - Isolated and unoptimized yields of E/Z mixtures.

General Procedure for the Synthesis of Oximes.

The synthesis of 9-anthracenylacetaldoxime is representative of the procedure employed. ω-(Nitrovinyl)anthracene (1.25 g, 5 mmol), $SnCl_2 \cdot 2H_2O$ (2.25 g, 10 mmol) and ethyl acetate (25 mL) were placed in a 50 mL Erlenmeyer flask and the mixture stirred at room temperature. A mildly exothermic reaction ensued which was accompanied by the gradual disappearance of the yellow coloration (nitroalkene). The reaction mixture was carefully poured into ice water and the solution made slightly basic (PH 7-8) by addition of 5% aqueous sodium bicarbonate. The product was extracted into ether, washed with brine, dried (Na_2SO_4) and the solvent removed under reduced pressure to yield essentially pure E/Z misture of 9-anthracenylacetaldoxime, m.p. 177-80°C. (1.05 g, 90%); ^{1}H-NMR (DMSO-d_6) δ 11.55 (s, 1H, =NOH, D_2O exchangable), 8.18-7.26 (m, 9H, Ar-H); 7.53 (dt, 2H, Z, Ar$\underline{CH_2}$-) 6.76 (t, 2H, E, Ar$\underline{CH_2}$-); 4.72, 4.55 (d, 2H, Z/E, -$\underline{CH_2}$-); ^{13}C-NMR (DMSO-d_6) δ 148.0, 147.8 (Z/E, -$\underline{CH}$=NOH), 28.0, 24.2 (E/Z, -$\underline{CH_2}$-).

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