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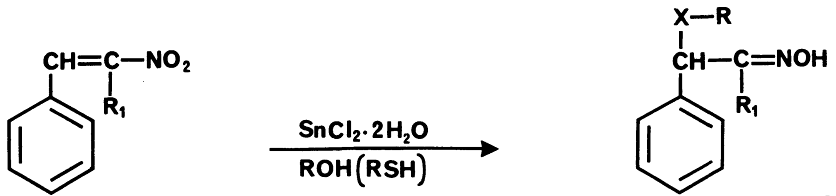
REDUCTION OF NITROALKENES WITH STANNOUS CHLORIDE IN NON-ACIDIC AND NON-AQUEOUS MEDIUM. SYNTHESIS OF α-SUBSTITUTED OXIMES

Rajender S. VARMA and George W. KABALKA*
Department of Chemistry, University of Tennessee,
Knoxville, Tennessee 37996-1600, U.S.A.

α,β-Unsaturated nitroalkenes are readily reduced by $SnCl_2 \cdot 2H_2O$ in alcoholic media to the α-alkoxy oxime derivatives in high yields. In the presence of ethanethiol, the corresponding α-alkylthio oximes are formed.

We have been investigating$^{1-2)}$ the potential utility of nitroalkenes for the rapid synthesis of amphetamine derivatives.$^{3)}$ It was recently reported$^{4)}$ that functionally substituted aromatic nitro compounds are readily reduced to the corresponding amines by tin(II) chloride in non-acidic media. The mildness of the reaction prompted us to explore the utility of this reagent for the reductions of conjugated nitroalkenes. We wish to report a new, rapid, high yield synthesis of α-substituted oximes using $SnCl_2 \cdot 2H_2O$ in alcoholic media.



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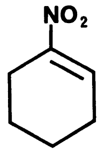
2	R	R1	X
a	CH_3	CH_3	O
b	C_2H_5	CH_3	O
c	C_2H_5	CH_3	S
d	CH_3	H	O
e	C_2H_5	H	O
f	C_2H_5	H	S



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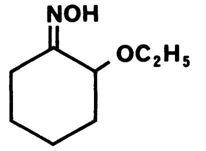

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The experimental procedure is straightforward. The alcohol or thiol (15 mL) was added to a mixture of nitroalkene (4 mmol) and stannous chloride (6 mmol) and then the reaction mixture was stirred at room temperature. A mildly exothermic reaction ensued which was accompanied by the disappearance of yellow coloration (nitroalkene). After 20 min, the reaction mixture was carefully poured onto ice. The pH of the solution was adjusted to ≈8 via the addition of 5% aqueous sodium bicarbonate and then the product was extracted into ether. The organic phase was washed with brine, dried ($MgSO_4$) and the solvent removed under reduced pressure to yield an essentially pure product.$^{5)}$ Chromatography on silica gel (5% ether/petroleum ether) provided analytically pure samples.$^{6)}$

The simplicity, fast rate, and high yield make this an attractive route for the preparation of oxime derivatives.8) Our results are summarized in Table 1.

Table 1.

No.	Yield a)	^{1}H-NMR(CDCl$_3$, δppm)		^{13}C-NMR(CDCl$_3$, δppm)			Analysis (Calculated)		
	%	CH	XC$_2$H$_5$/CH$_3$	CH	XCH$_2$/CH$_3$	CH$_3$	C	H	N/S
2a	89	4.87(s)	3.40(s)	83.70	56.76	9.03	68.46 (68.39)	7.72 (7.77)	7.13 (7.25)
2b	90	4.93(s)	3.53(q), 1.27(t)	81.97	64.59	9.17	63.36 (67.04)	7.57 (7.26)	7.74 (7.82)
2c	90	4.70(s)	2.48(q), 1.24(t)	53.50	25.53	11.42	62.81 (63.16)	7.14 (7.18)	15.58 (15.31)
2d	83	4.80(d) b)	3.37(s)	80.51 c)	56.76	-	65.81 (65.45)	6.74 (6.67)	8.67 (8.48)
2e	86	4.92(d) b)	3.50(m), 1.23(t)	78.73 c)	64.50	-	66.79 (67.04)	7.01 (7.26)	8.39 (7.82)
2f	71	4.58(d) b)	2.54(m), 1.25(m)	47.82 c)	25.58	-	61.29 (61.54)	6.69 (6.67)	16.59 (16.14)
4	85	3.85(m) d)	3.44(m), 1.18(m)	-	-	-	61.16 (61.15)	9.42 (9.55)	8.74 (8.92)

a) Isolated and unoptimized yields; all products are thick oils. b) The data presented are for the E-isomer; the benzylic hydrogens for the minor Z-isomer appear as doublets at 5.53 (2d), 5.66 (2e), and 5.5 (2f). c) The values are for the E-isomer; the resonance of the benzylic carbon in the Z-isomer appears at 75.47 (2d), 73.63 (2e), and 41.24 (2f). d) The data presented are for the E-isomer; the corresponding Z-isomer (minor) exhibits this resonance at 4.96.

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References

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5) Single isomers were obtained when β-methyl-β-nitrostyrene derivatives were reduced. Although the products were not completely characterized, steric arguments coupled with the high field (^{13}C-NMR) position of the terminal methyl group (≈9 ppm) in each of the products support the postulation that the oxime possesses the E-configuration. Spectral analyses of the products from the reduction of unsubstituted β-nitrostyrene indicate that a mixture of E- and Z-isomers are formed.

6) Further confirmation of the structure of the products was provided by the hydrolysis7) of oxime 2b to 1-ethoxy-1-phenylpropanone: IRν_{max} 1710 cm^{-1}; ^{1}H-NMR (CDCl$_3$)δ: 7.36(m,5H,Ar-H), 4.75(s,1H,CH), 3.48(q,2H,CH$_2$), 2.12(s,3H, -COCH$_3$), 1.2(t,3H,CH$_3$).

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8) It has been reported9) that α-alkoxy oximes are isolated from product mixtures in modest yields when nitroalkenes were reduced under acidic conditions with SnCl$_2$·2H$_2$O.

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