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REACTIONS OF β-NITROSTYRENES WITH STABILIZED NUCLEOPHILES

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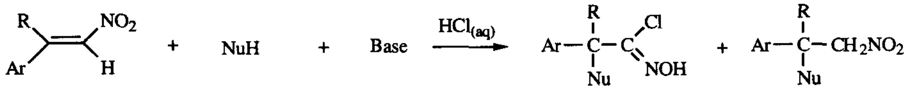
Abstract: β-Nitrostyrenes **1** react with stabilized nucleophiles to generate hydroximoyl chloride **2** after workup with ice cold concentrated hydrochloric acid. One-pot synthesis of five-membered carbocycles or cyclic ethers from the Michael addition of the carbon nucleophiles or alkoxides to the β-nitrostyrenes is reported. © 1997 Elsevier Science Ltd.

Our previous study find that high yields of hydroximoyl halides or nitrile oxides generated when β-nitrostyrenes react with nonstabilized organometallic reagent such as Grignard reagents and workup with ice cold concentrated hydrohalic acids.[1] According to literature reports,[1,2] we predict hydroximoyl halides also could be generated when β-nitrostyrenes react with stabilized nucleophiles and workup under similar conditions. In this paper, we wish to report β-nitrostyrenes **1** react with carbon nucleophiles, alkoxides or (EtO)$_2$PO$^-$ to generate medium to high yields (60-98%) of hydroximoyl chlorides **2** and nitroalkanes **3** (eq 1) after add the nitronates to the ice cold concentrated hydrochloric acid[3] and the mechanism is proposed to be similar to previous report.[1]



(1)

1			2	3
1b	$CH_2(CO_2Et)_2$	NaH	75%	20%
1b	$C_6H_5COCH_3$	LDA	60%	-
1b	$HCCCH_2OH$	NaH	68%	30%
1c	$HCCCH_2OH$	NaH	75%	-
1a	$(EtO)_2POH$	NaH	95%	-
1b	$(EtO)_2POH$	NaH	75%	-
1d	$(EtO)_2POH$	NaH	98%	-

a: Ar = R = Ph
b: Ar = Ph, R = H
c: Ar = 4-FC_6H_4, R = H
d: Ar = 4-MeC_6H_4, R = H
e: Ar = 2-thienyl, R = H
f: Ar= 2-furyl, R = H

It is known that nitrile oxides can undergo 1,3-dipolar cycloaddition with olefins or alkynes to generate 2-isoxazoline or isoxazole respectively.[2] One-pot synthesis of [3, 3, 0] bicyclic compounds **4-6** by adding the nitronates to the ice cold concentrated hydrochloric acid, extraction with dichloromethane and dehydrochlorination by little excess triethylamine is shown as the following equations 2-4.

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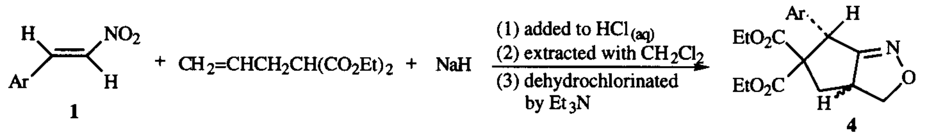
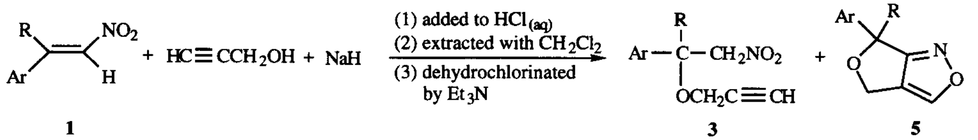


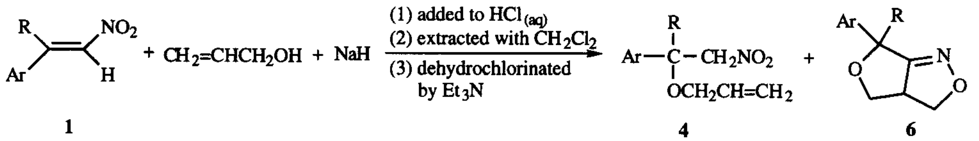
(2)

	4
1b: Ar = Ph	60% (*cis*), 8% (*trans*)
1d: Ar = 4-MeC$_6$H$_4$	75% (*cis*), 10% (*trans*)
1e: Ar = 2-thienyl	60% (*cis*), 17% (*trans*)
1f: Ar = 2-furyl	61% (*cis*), 24% (*trans*)



(3)

1	3	5
1a: Ar = R = Ph	15%	60%
1c: Ar = 4-FC$_6$H$_4$, R = H	–	60%



(4)

1	4	6
1a: Ar = R = Ph	30%	64%
1c: Ar = 4-FC$_6$H$_4$, R = H	–	61%

References and Notes

1. Yao, C.-F.; Chen, W.-C.; Lin, Y.-M. *Tetrahedron Lett.* **1996**, 37, 6339.
2. (a) Wade, P. A.; Amin, N. V.; Yen, H.-K.; Price, D. T.; Huhn, G. F. *J. Org. Chem.* **1984**, 49, 4595-4601. (b) Torsell, K. B. G. *Nitrile Oxides, Nitrones, and Nitronate in Organic Synthesis* 1988, VCH, New York. (c) Dehaen, W.; Hassner, A. *Tetrahedron Lett.* **1990**, 31, 743. (d) Hassner, A.; Dehaen, W. *J. Org. Chem.* **1990**, 55, 5505. (e) Hassner, A.; Dehaen, W. *Chem. Ber.* **1991**, 124, 1181. (f) Gottlieb, L.; Hassner, A. *J. Org. Chem.* **1995**, 60, 3759. (f) Namboothiri, I. N. N.; Hassner, A.; Gottlieb, H. E. *J. Org. Chem.* **1997**, 62, 485.
3. The general procedure is to add **1b** (4 mmol) in 20 mL THF to 8 mmol of the diethylphosphite with 10 mmol NaH in 30 mL of THF at 0 °C. Within 10 minutes, the solution is slowly added to ice cold concentrated hydrochloric acid (37%). After stirring 30 minutes, the solution is extracted with dichloromethane and the organic layer is washed with brine, dried over anhydrous MgSO$_4$, filtered and concentrated to give oily mixture. The crude NMR indicates that the mixture contains 75% yield of product by using CH$_2$Br$_2$ as internal standard. Flash column chromatography is used to purify the mixture to obtain pure product by using hexane-ethyl acetate as eluent. MP 117-118 °C; ^{1}H-NMR (200MHz, CDCl$_3$) δ 11.58 (s br, 1H), 7.44-7.33 (m, 5H), 4.24 (quint d, *J* = 7.2, 1.0, 2H), 4.20 (d, *J* = 26.4, 1H), 4.07-3.89 (m, 1H), 3.88-3.69 (m, 1H), 1.32 (t, *J* = 7.2, 3H), 1.09 (t, *J* = 7.2, 3H); ^{13}C-NMR (50MHz, CDCl$_3$) δ 133.02, 131.85 (d, *J* = 7.6), 129.80 (d, *J* = 6.0), 128.70 (d, *J* = 2.3), 128.32 (d, *J* = 2.3), 63.79 (d, *J* = 6.9), 63.55 (d, *J* = 6.9), 53.27 (d, *J* = 139.6), 16.27 (d, *J* = 6.0), 16.01 (d, *J* = 6.0). HRMS calculated for $C_{12}H_{17}O_4NClP$ ((M+2)$^+$) 307.0554, found 307.0565; (M$^+$) calculated 305.0550, found 305.0559. Elemental analysis calculated C: 47.15, H: 5.61, N: 4.58; found C: 47.25, H: 5.46, N: 4.59.

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