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REACTIONS OF β-NITROSTYRENES WITH STABILIZED NUCLEOPHILES

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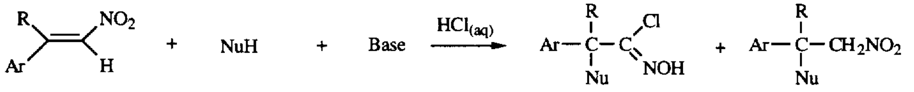
Abstract: β-Nitrostyrenes **1** react with stabilized nucleophiles to generate hydroximoyl chloride **2** after workup with ice cold concentrated hydrochloric acid. One-pot synthesis of five-membered carbocycles or cyclic ethers from the Michael addition of the carbon nucleophiles or alkoxides to the 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 $(EtO)_2PO^-$ 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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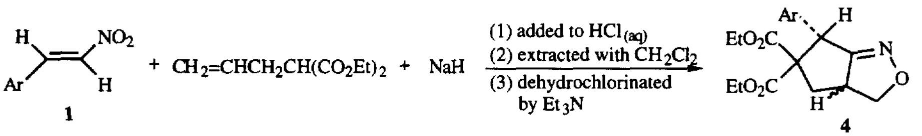
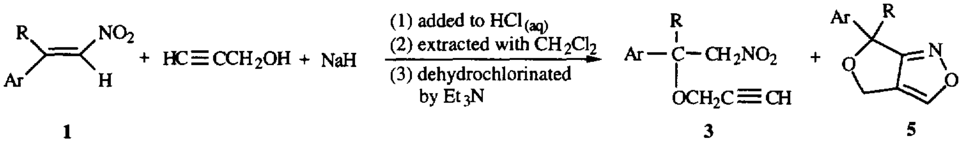


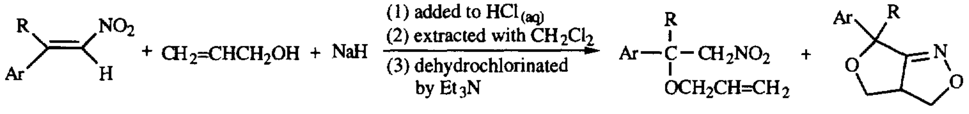
(2)

1	4
1b: Ar = Ph	60% (*cis*), 8% (*trans*)
1d: Ar = 4-MeC_6H_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_6H_4, R = H	–	60%



(4)

1	4	6
1a: Ar = R = Ph	30%	64%
1c: Ar = 4-FC_6H_4, R = H	–	61%

References and Notes

1. Yao, C.-F.; Chen, W.-C.; Lin, Y.-M. *Tetrahedron Lett.* **1996**, 37, 6339.
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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_2Br_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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