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Direct Carbohydroximoylation of Aromatics with Primary Nitroalkanes in Triflic Acid (TFSA).

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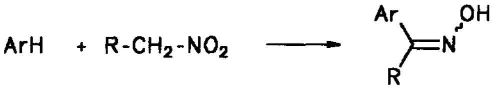
Abstract: Primary nitroalkanes react with aromatics in triflic acid to yield arylated oximes at 70-80°C.

In acids (HF, H_2SO_4, TFSA, TFSA-TFA) and at low temperature, aromatics react with α,β-unsaturated nitroderivatives,[1-4] α-carbonylnitromethanes[5,6] and nitronates of nitroalkanes[7,8] to yield arylated oximes. No reaction was observed with nitroalkanes under similar experimental conditions.

We would like to report that oximes can be obtained in fair to excellent yields when primary nitroalkanes are reacted with aromatics in triflic acid (TFSA) at 70-80°C.



In a typical procedure, a solution of nitroethane (0.5 ml; 7 mmol) in benzene (2 ml; 22 mmol) was slowly added to triflic acid (4 ml). The whole, maintained under an atmosphere of nitrogen, was magnetically stirred for 16hr at 75°C. After cooling at ambiant temperature, and usual work-up, the residue was flash-chromatographed over silica gel (AcOEt : n-hexane 10 : 90) to afford E-acetophenone oxime (15 mg; 1.6%) m.p. 59°C (Lit[9] 59°C) and Z-acetophenone oxime (900 mg; 95%) m.p. 83°C (Lit[9] 83°C).

The Z isomers of the oximes are the primary products of the reaction[7,8]. Oximes formed with nitroethane and nitropropane are stable in the reaction conditions but Z-benzaldoxime isomerizes rapidly to yield a mixture of stereoisomeric oximes.[8,10] (Table 1)

Table 1. Reaction of benzene with nitroalkanes

Nitroalkane	Oxime (E+Z) (Yield%)*	Z (%)
CH_3NO_2	75	33
$CH_3CH_2NO_2$	96	98
$CH_3CH_2CH_2NO_2$	85	>95**

*Based on nitroalkane; ** The E isomer was not detected by ^1H NMR

This new reaction can be extended to other aromatics with similar stereoselectivity.(Table 2)

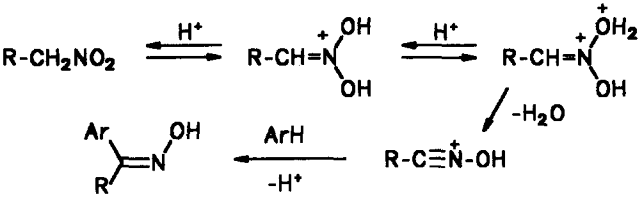
Regioselectivity is in agreement with an electrophilic aromatic substitution, but the reaction fails for strongly deactivated aromatics (nitrobenzene, benzonitrile[11]), reflecting a poor reactive species.

Table 2. Reactions of Aromatics with Nitroalkanes

Aromatic	Nitroalkane	Oxime (E+Z) (Yield %)*	ortho/para
Toluene	CH_3NO_2	75	35/65
	$CH_3CH_2NO_2$	82	40/60
Fluorobenzene	CH_3NO_2	34	10/90
	$CH_3CH_2NO_2$	44	15/85
Anisole	CH_3NO_2	36	50/50
	$CH_3CH_2NO_2$	34	0/100
Naphtalene	CH_3NO_2	20	88/12**
	$CH_3CH_2NO_2$	84	95/05**

*based on nitroalkane; ** α/β ratio

The postulated mecanism is similar to what we proposed previously to account for the reaction of nitronates and α-carbonylnitromethanes with aromatics.[6,8] It implies the intermediacy of a protonated nitronic acid, precursor of the corresponding hydroxynitrilium ion[12] which is the reactive species.



It should be pointed out that no conversion to amides *via* a Beckmann rearrangement was observed, oximes being exclusively N-protonated in triflic acid.[10]

References and notes

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11. Only trimerization of C_6H_5CN was observed with TFSA to yield triphenyltriazine.
12. Such an hydroxynitrilium ion has been fully characterized by ^1H and ^{13}C NMR spectroscopy from $(CH_3S)_2C=CHNO_2$; Coustard, J.M.; Jacquesy, J.C. *Phosphorus, Sulfur, Silicon; special isssue 15th ISOCS* **1992**, in press.

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