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A Facile Conversion of Nitro Olefins to Functionalised Hydroximoyl Chlorides As Nitrile Oxide Precursors[#]

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Abstract:*Hydroximoyl chlorides bearing α-chloro functionality were prepared from conjugated nitro olefins using $TiCl_4$ at room temperature in moderate to good yields.*

Nitrile oxides are important tools in synthetic organic chemistry, since they readily undergo a variety of 1,3 dipolar cycloadditions[1]. The heterocycles *viz* isoxazolines and isoxazoles formed respectively from olefinic and acetylenic compounds with nitrile oxides have great synthetic utility[2], since a number of functionalities are masked in these rings. For increasing the versatility of the heterocycles formed from nitrile oxides, functionalities have been introduced in the dipolarophiles. However, only few such changes have been reported in the case of dipoles[3].

Several methods have been described in literature for the *in situ* generation of nitrile oxides[4], amongst which Mukaiyama's[5] dehydration of primary nitro compounds with phenyl isocyanate and Huisgen's[6] base induced dehydrohalogenation of hydroximoyl chlorides are the frequently used. Usually hydroximoyl chlorides are prepared by chlorination of the corresponding oximes, for which number[7] of chlorinating reagents have been employed for improving the yield, simplifying the experimental conditions and avoiding polyhalogenation. To the best of our knowledge, there is no report for the synthesis of hydroximoyl chlorides from conjugated nitro olefins. In this communication, we wish to report a facile method for the synthesis of hydroximoyl chlorides bearing an α-chloro functionality from conjugated nitro olefins using $TiCl_4$[8]. The reaction proceeds at ambient temperature with moderate to good yields.

A typical experimental procedure is as follows. To a stirred solution of ω-nitrostyrene (**1d**) (0.01mole) in dry CH_2Cl_2 (10ml), was added dropwise a slight excess of $TiCl_4$ (0.012mole, 1M solution in CH_2Cl_2) at room temperature. The resulting mixture was stirred for 1h and usual workup gave spectroscopically pure α-chloro phenylaceto hydroximoyl chloride (**6d**) purified by crystallization and identified by elemental analysis, M^+ ion, IR, ^1H NMR and further confirmed by preparing isoxazoline derivative[9].

A plausible mechanism is suggested by an initial elctrophilic attack of $TiCl_4$ on nitro olefin (**1**) leading to **3**, formed by chlorine transfer to the intermediate (**2**). **3** gives α-halo nitroso derivative (**5**) *via* **4** by loss of $TiOCl_2$ and chlorine transfer. **5** then isomerises[7(a)] to hydroximoyl chlorides(**6**) (**scheme**).

SCHEME

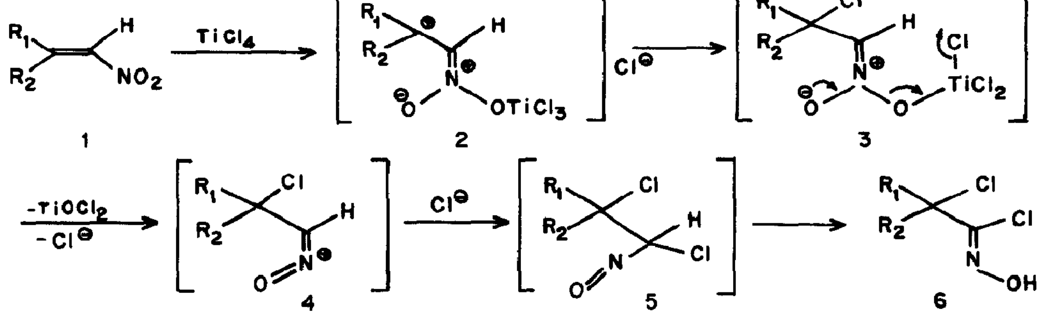

Table:Preparation of α-chloro hydroximoyl chlorides 6a-g.

Compd No	R_1	R_2	m.p(°c)	Isolated Yield(%)
6a	Isopropyl	H	Oil	68
6b	Methyl	Methyl	Oil	64
6c	Cyclo hexyl		51-52	65
6d	C_6H_5	H	79	78
6e	4-ClC_6H_4	H	96	80
6f	4-FC_6H_4	H	84	82
6g	4-$NO_2C_6H_4$	H	114	72

The reaction thus offers an useful route to hydroximoyl chlorides with α-chloro functionality from conjugate nitro olefins, which could be readily obtained from aldehydes/ketones with nitromethane.

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8. For acylmethylation of aromatic compounds by reaction of conjugated nitro olefins with aromatic compounds using $TiCl_4$ *cf* Lee, K.; Oh, D.Y. *Tetrahedron Lett.*, **1988**, *29*, 2977-2978.
9. All new compounds described here gave satisfactory IR, ^1H NMR, elemental analysis and/or Mass spectra. Cycloaddition of nitrile oxide generated from **6d** with ethyl acrylate gave diastereomeric isoxazolines in 56% yield, identified by IR, ^1H NMR and ^{13}C NMR.

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