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Solid-Phase Synthesis of Oximes

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Solid-Phase Synthesis of Oximes

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Abstract: In an extremely fast, high efficient and novel method, the reaction of hydroxylamine hydrochloride with a number of aldehydes and ketones under solventless 'dry' condition gave oximes in quantitative yield

The oximes are highly crystalline and efficient for characterisation and purification of carbonyl compounds. These compounds represent a convenient series of derivatives of carbonyl compounds and may be used as intermediates for the preparation of amides by the Beckmann rearrangement [1] nitrones, [2] hydroximinoyl chlorides, [3] nitrile oxides [3] and chiral α-sulfinyl oximes. [4] The usual method for preparation of oximes involves treatment of carbonyl

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compounds with hydroxylamine hydrochlorides in a basic aqueous medium with adjustment of pH. Some oximes are liquid or oil-out because of improper levels of solvent or reactant, being used, the operating conditions of this method are difficult.

Since the early work of Toda, [5] application of solid state organic chemistry has been currently under intensive investigation. and has been recently reviewed. [6] The observation obtained were: a) decreasing reaction time b) cleaner reaction with easier work-up. 5-7

In this article, we intend to report that silica gel, [8] in the presence of NaOH, could be used as an useful catalyst for preparation of oximes in dry media . Hydroxylamine hydrochlorides were reacted with several aromatic aldehydes and ketones (see table 1) yielding the desired oximes in quantitative amounts.

The ability of silica gel [8] in dry media was demonstrated using various aldehydes and ketones with hydroxylamine hydrochloride in the presence of a base, the resulting data are summarised in Table 1. The aromatic aldehydes were converted to the corresponding oximes more than 95 % yield in less than 3 min. (entries a-k). In the case of ketones reactions were more difficult and completed between 6-8 min. with lower yields (entries l-s), and the less reactive benzophenone was also found to condense with hydroxylamine hydrochloride in 75 % yield in 8 min. (entry r).

In order to evaluate the influence of silica gel, the reaction of benzaldehyde and hydroxylamine hydrochloride without silica gel was tested. The results were unsuccessful and the aldehyde unchanged after 20 min. of grinding thoroughly in a mortar. Only in the case of dry media with silica gel, the oxime was produced in excellent yield.

Another important observation found in this method is the exclusive reaction of aldehydes with hydroxylamine hydrochloride irrespective of the presence of ketones. This was carried out by treating one equivalent of aldehydes in the presence of one equivalent

of ketones with two equivalent of hydroxylamine hydrochloride, only the aldehydes selectively converted to corresponding oximes and the ketones did not react at all (Scheme 1). Therefore, this methodology could be used selectively for the preparation of aldoximes of the compounds that contain both aldehyde and ketone functional groups.

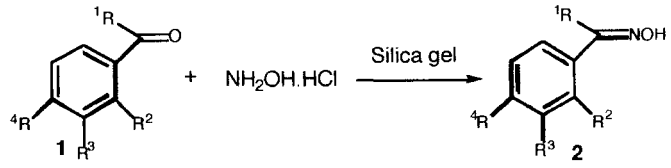
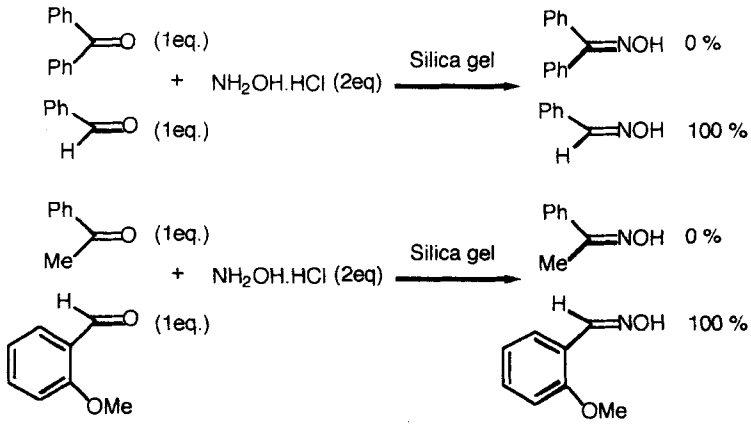


Table 1. Reaction of carbonyl compounds **1** with hydroxylamine hydrochloride.

Entry 1	R^1	R^2	R^3	R^4	Time (min)	Yield % a, b
a	H	H	H	H	2	98
b	H	OMe	H	H	2	100
c	H	Cl	H	H	3	95
d	H	H	Cl	H	3	95
e	H	H	H	Cl	3	95
f	H	H	H	NO_2	2	98
g	H	H	NO_2	H	4	90
h	H	H	OMe	OMe	2	96
i	H	OH	H	H	3	90
j	H	Br	H	H	3	95
k	H	H	H	Br	3	95
l	Me	H	H	H	6	90
m	Me	Br	H	H	6	85
n	Me	H	H	Br	6	90
o	Me	H	H	Cl	7	95
p	Me	H	NO_2	H	6	90
q	Me	H	H	NO_2	6	95
r	Ph	H	H	H	8	75
s	Ph	H	H	Cl	8	85

a) Evaluated by weight of isolated oxime after purification.

b) All products are known compound and exhibit satisfactory spectroscopic data (^{1}H NMR and I.R.)



Scheme 1.

To the best of our knowledge this is the first example for silica gel catalysis of this reaction. In conclusion, the reported procedure is an interesting , easy and novel method for the preparation of oximes. These reactions were fast, the procedure was simple and of low cost, and it was possible to work under mild conditions.

Experimental

In a typical experiment, a mixture of 0.106 g (1 mmol) of benzaldehyde and (2 mmol, 0.140 g) of hydroxylamine hydrochloride was ground thoroughly in a mortar and supported on silica gel [7] (1 g). The reaction mixture was grinding for 2 min. (table 1) and the completion of the reaction is monitored by TLC examination. After completion of the reaction, the mixture was cooled to room temperature, 10 ml of 5% aqueous HCl was added. The mixture was extracted with CH_2Cl_2 (2x5 ml). The extracts were combined and dried ($CaCl_2$), evaporation of solvent under vacuum gave benzaldehyde oxime, which was ≥98 pure, (TLC, 1H NMR). The product could be further purified by recrystallization from n-hexane.

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8. Silica gel 60, Fluka, particle size 0.2-0.5 mm (35-70 ASTM.

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