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A CLEAN CLAY CATALYSED SYNTHESIS OF α,N-DIARYLNITRONES

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ABSTRACT

The first clean and the facile clay catalysed synthesis of α,N-diarylnitrones in good yield is reported.

α,N-Diarylnitrones are synthesised by several methods,[1] the most popular method being the condensation of arylaldehydes with the arylhydroxylamines.[2] This condensation, which is usually carried out in ethanol requires warming the reaction mixture or even refluxing in some cases. Under such circumstances, the formation of dimeric by-product of the hydroxylamine, namely diazobenzene, is unavoidable. Also the rate of condensation varies widely with the nature of the substituents in the aryl part of the aldehyde or

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hydroxylamine. Thus this method, though normally gives better yields, is impaired by the above facts. Hence any other modified methodology which overcomes the above drawbacks is worth considering. In view of this and in continuation of our work on the synthetic utility of clay catalysed reactions[3,4] and nitrones,[5] we planned to carry out the condensation of arylaldehyde with phenylhydroxylamine in presence of K10-Montmorillonite, a clay medium. It may be mentioned that the clay K10-Montmorillonite has already been employed in acid catalysed aromatic substitutions,[6] aldol condensation[7] and rearrangement reactions.[8] These methods enjoy advantages such as (a) easy handling, (b) recovery of catalyst, (c) greater chemo/regio selectivity etc.

In this method, a well ground mixture of arylaldehyde, phenylhydroxylamine and clay standing at room temperature for 2h results in nitrones **1** and the yield and melting point of the isolated nitrones are given in the **Table** . It can be seen from the **Table** that the yield of the nitrones is generally good ranging from 73-85%. Probably this is one of the first synthesis of nitrones employing a clay medium. It should be mentioned that a mineral acid catalysed condensation of benzaldehyde and phenylhydroxylamine does not lead to the formation of nitrone under normal conditions. Hence, though this clay is acidic, efficient condensation takes

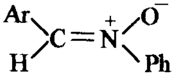
Table: Yield and melting point of the synthesised nitrones*

Compound	Melting point (°C)	Yield (%)
1a	114	85
1b	162	75
1c	153	82
1d	140	81
1e	118	76
1f	94	78
1g	150	78
1h	187	80
1i	116	79
1j	92-93	73
1k	130	73
1l	138	79

*All the compounds (**1a** - **1h**,[10] **1i**,[11] **1j**,[12] **1k**,[13] and **1l**,[14]) are known. Products were characterised by comparision with IR and NMR spectral data of the authentic samples. For compounds **1j**, **1k** and **1l** the IR and NMR spectra are similar to that of the other compounds.

place in this medium, avoiding the formation of diazobenzene or Bamberger rearrangement which is expected to take place under acidic conditions with arylhydroxylamines. It is interesting to note that the same reaction when carried out at elevated temperature i.e., on a water bath for 2h, does not result in the nitrone. The product isolated was identified as azoxybenzene by HPLC, IR, ^{1}H & ^{13}C NMR and mass spectra. Any change in the clay composition or time, does not have any effect on the product formation, though a slight change in the product yield is noticed. Whatever be the aldehyde, this reaction results in azoxybenzene as the major product.

Nitrones prepared by the conventional procedures[2] when treated with the clay and kept at the above experimental conditions undergo the same fate, though not at room temperature, giving azoxybenzene. Hence, at high temperature, the initially formed nitrone would have undergone hydrolysis to give N-phenylhydroxylamine, which might have been converted into azoxybenzene. The acid catalysed hydrolysis must have been effected by water molecules present in the clay, which is well known for its Bronsted behaviour. The support for this observation comes from the fact that even at room temperature when phenylhydroxylamine alone was mixed with clay it was converted into azoxybenzene. This is in contrast to the acid catalysed Bamberger rearrangement observed in arylhydroxylamines upon treatment with mineral acids. Hence it is concluded that the clay treated condensation of arylaldehyde and arylhydroxylamine at room temperature is a method of choice for the preparation of α,N-diaryl nitrones in fairly good yield without any by-products.



1

a)Ar = Phenyl
b)Ar = 4-Bromophenyl
c)Ar = 4-Chlorophenyl
d)Ar = 4-Dimethylaminophenyl
e)Ar = 4-Methoxyphenyl
f)Ar = 4-Methylphenyl
g)Ar = 3-Nitrophenyl
h)Ar = 4-Nitrophenyl
i)Ar = 2-Hydroxyphenyl
j)Ar = 2-Furyl
k)Ar = 1-Naphthyl
l)Ar = 3,4-Methylenedioxyphenyl

EXPERIMENTAL

General Procedure for the Preparation of α-Aryl-N-phenyl nitrones 1 using Clay.

A mixture of arylaldehyde (0.01 mol), phenylhydroxylamine (0.01 mol), obtained by the reduction of nitrobenzene by zinc and ammonium chloride,[9] and clay (1:1 w/w mixture with respect to phenylhydroxylamine) was thoroughly mixed and kept at the room temperature for 2h. The mixture was then extracted with chloroform. Evaporation of the solvent gave a semisolid which was crystallised from ether and identified as the nitrone by mixed melting point and spectral data. The above mixture when kept on a boiling water bath for 2h yielded azoxybenzene (~45%).

A mixture of phenylhydroxylamine (0.01 mol) and the clay (1:1 w/w mixture) was throughly mixed and kept at room temperature for an hour. The mixture was then extracted with chloroform and evaporation of the solvent gave azoxybenzene (90%).

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