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Ruthenium catalysed imidation of aldehydes using PhI=NTs as imido transfer reagent

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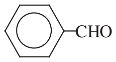
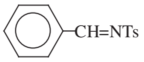
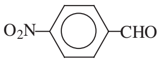
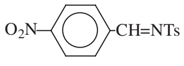
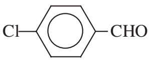
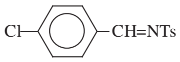
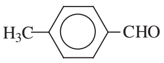
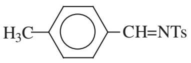
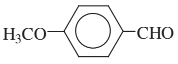
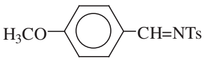
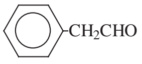
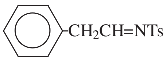
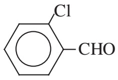
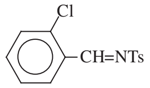
The [*N*-(*p*-tolylsulfonyl)imino] phenyliodinane (PhI=NTs) was found to be an efficient reagent for imidation of variety of aldehydes using [$RuCl_2(PPh_3)_3$] as catalyst in the presence of triphenylphosphine.

Keywords: aldehyde, imidation, ruthenium, PhI=NTs

The use of imido-metal complexes (M=NTs) formed *in situ* from metal complexes and nitrene precursors has become a powerful tool for the aziridination of alkenes, amidation of alkanes and allylic amination of alkenes.[1] In recent years [*N*-(*p*-tolylsulfonyl)imino] phenyliodinane (PhI=NTs)[2] has been found to be a very convenient nitrene precursor and has been widely used for the aziridination of a variety of alkenes[3] and amination[4] reactions in the presence of several transition metal based catalysts. However, the potential of PhI=NTs for the imidation of aldehydes does not appear to have been explored in the literature. Imination of carbonyl compounds is an important synthetic transformation[5] as imines in general and *N*-tosyl imines in particular are very important and versatile synthetic intermediates that are able to undergo a plethora of organic synthesis.[6] A variety of methods for the preparation of *N*-tosyl imines have been reported in the literature[7] but most of these suffer from drawbacks such as the lower yields of the products, harsh reaction conditions and longer reaction times.

Herein we report first catalytic method for the imidation of aldehydes with PhI=NTs in the presence of triphenylphosphine using [$RuCl_2(PPh_3)_3$] as catalyst to yield *N*-tosyl aldimines in excellent yields (Scheme 1).

Table 1 Ruthenium catalysed imidation of aldehydes by PhI=NTs [a]

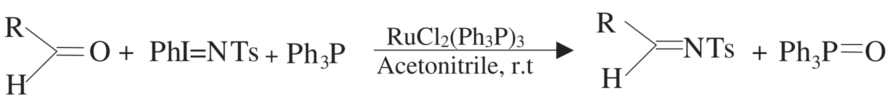
Entry	Aldehyde	Product	Reaction Time /h	Yield[b]
1			8	75
2			4.5	85
3			5	80
4			12	80
5			14	70
6			20	40
7			7.0	75

[a] *Typical experimental procedure for imidation of aldehydes:* To a stirred suspension of benzaldehyde (1 mmol, 106 mg), PhI=NTs (1 mmol, 373 mg) and triphenylphosphine (1.2 mmol, 314 mg) in dry acetonitrile (5 ml) was added [$RuCl_2(Ph_3P)_3$] (0.05 mmol, 5 mol%) under dinitrogen at room temperature (20° C). Stirring was continued for 8 h. (completion of the reaction was indicated by complete dissolution of PhI=NTs). The solvent was evaporated under vacuum and the residue thus obtained was purified by passing through the silica gel column using hexane/ethylacetate (9:1) as eluent. Evaporation of the solvent yielded corresponding benzylidine *N*-(*p*-tolylsulfonyl)imine (194 mg, 75 %) which was identified by comparing the physical and spectral data with those of authentic sample.[9] Similarly the imidation of other aldehydes was carried out and their reaction times and yields are given.

[b] Isolated yields.

Imidation of a variety of aldehydes was carried out by treating them with PhI=NTs in presence of triphenylphosphine using a catalytic amount of [$RuCl_2$ $(PPh_3)_3$] at room temperature under very mild conditions. These results are presented in Table 1 and clearly indicate that among the various aromatic aldehydes studied, those substituted with electron withdrawing groups (Table 1, entries 2,3,7) were found to be more reactive and required shorter reaction times. The presence of triphenyl phosphine was found to be essential and the reaction did not proceed in its absence. When the ruthenium catalysed imidation of benzaldehyde was carried out using styrene as the reductant in place of triphenylphosphine, no imidation of benzaldehyde was observed and *N*-(p-tolylsulfonyl)-2-(phenyl)aziridine was obtained in 85% yield, indicating that styrene was more reactive with PhI=NTs under these catalytic conditions than benzaldehyde. The imidation of benzaldehyde was also carried out with copper acetylacetonate in place of [$RuCl_2(PPh_3)_3$] as catalyst and the yield of PhCH=NTs was found to be very poor, indicating that the copper complex is a very poor catalyst for the imidation of aldehydes, contrary to its use in aziridination. This could probably be due to the comparative ease of formation of oxo-ruthenium-species from the reaction of ruthenium-nitroid (Ru=NTs) with aldehyde than in the case of a copper-nitroid (Cu=NTs). These reactions were associated with the formation of *p*-toluenesulfonamide as a by-product and the presence of 5Å molecular sieves in the reaction mixture showed significant decrease in *p*-toluenesulfonamide formation.

Although the mechanism of this reaction is not clear at this stage, the reaction probably involves the formation of Ph_3P=NTs from Ph_3P and PhI=NTs[8] followed by imido-



Scheme 1

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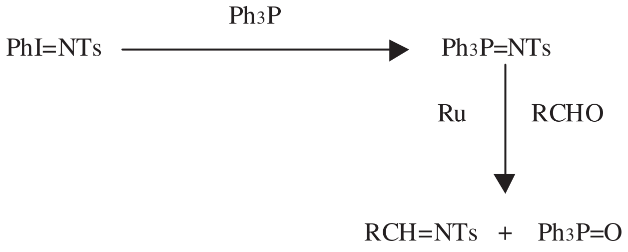

Scheme 2

transfer / aza-wittig reaction with aldehyde in presence of the ruthenium catalyst (Scheme 2).

In conclusion, the present method describes a first catalytic method for the imidation of a variety of aldehydes using PhI=NTs as imido-transfer reagent. The better yields of the products, mild reaction conditions and easy preparation/ availability of the imido-transfer reagent make this a facile method for the imidation of aldehydes in excellent yields.

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