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Tetrahedron Letters

Tetrahedron Letters 45 (2004) 4341–4343

A novel imido-transfer reaction of aldehydes with $Ph_3P{=}NTs$ using $RuCl_2(PPh_3)_3$ as catalyst

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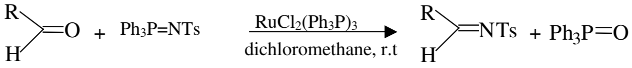
Received 4 March 2004; revised 25 March 2004; accepted 31 March 2004

Abstract—(*N*-Tosylimino)triphenylphosphorane ($Ph_3P{=}NTs$) was found to be an efficient imido-transfer reagent for the imidation of a variety of aldehydes using $RuCl_2(PPh_3)_3$ as the catalyst.

The development of metal mediated imido transfer reactions such as aziridination of alkenes, amidation of hydrocarbons and allylic amination of alkenes is an area of current interest.[1] In the recent years [*N*-(*p*-tolylsulfonyl)imino] phenyliodinane ($PhI{=}NTs$)[2] has emerged as a very useful nitrogen source and has been widely used for the aziridination[3] and amination of alkanes[4] in the presence of transition metal based catalysts. Recently Che and co-workers[1a] reported the reactions of imido-ruthenium complexes [Ru(porphyrin)-$(NTs)_2$] generated from [Ru{porphyrin(CO)(MeOH)}] and $PhI{=}NTs$ with alkenes and hydrocarbons to yield aziridination and amidation products, respectively, in good yields. However, there are drawbacks with the use of $PhI{=}NTs$ as a nitrogen source; it is difficult to prepare and isolate, expensive, yields iodobenzene in equimolar amounts and oxygenated hydrocarbons are dominant by-products. In efforts to develop a cheaper and more convenient nitrogen source as an alternative to $PhI{=}NTs$ the use of chloramine-T (*N*-chloro-*N*-sodio-*p*-toluenesulfonamide),[5] bromamine-T (*N*-bromo-*N*-sodio-*p*-toluenesulfonamide)[6] and *N*-iodo-*N*-potassio-*p*-toluenesulfonamide[7] have been described in the literature.

In this Letter we report a novel imido-transfer reaction of aldehydes using $RuCl_2(PPh_3)_3$ as the catalyst and (*N*-tosylimino)triphenylphosphorane ($Ph_3P{=}NTs$)[8] as the nitrogen source (Scheme 1). The imidation of a variety of aromatic and aliphatic aldehydes was carried out with $Ph_3P{=}NTs$ using a catalytic amount of $RuCl_2(PPh_3)_3$ in dichloromethane at room temperature under a nitrogen atmosphere.[9] All the aldehydes were converted smoothly to the corresponding aldimides in good yields. These results are presented in the Table 1 and indicate that amongst the aldehydes studied, aromatic aldehydes substituted with electron withdrawing groups were found to be the more reactive and required shorter reaction times. To evaluate the effect of the catalyst, a blank experiment was carried out using 4-nitrobenzaldehyde as the substrate under the usual reaction conditions but in the absence of catalyst. The reaction was not complete even after 12 h, and the yield of the product was very poor. The effect of different solvents such as dichloromethane, 1,2-dichloroethane, acetonitrile and toluene was also studied using 4-nitrobenzaldehyde under the standard reaction conditions. Amongst the various solvents studied, dichloromethane was found to be the best.



Scheme 1.

The exact mechanism of the reaction is not clear at this stage. It probably involves the formation of a ruthenium-imido intermediate from the reaction of $Ph_3P{=}NTs$ with the Ru complex followed by the transfer of the imido group to the carbonyl moiety to yield the corresponding aldimide as shown in Scheme 2. The appearance of triphenylphosphine as indicated by TLC during the reaction also supports the intermediacy of a ruthenium-imido complex.

Keywords: Imidation; Ruthenium; Aldehyde; $Ph_3P{=}NTs$.

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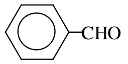
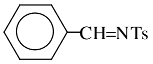
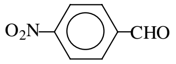
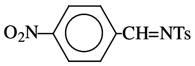
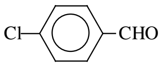
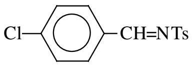
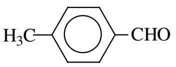
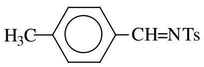
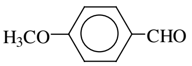
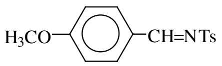
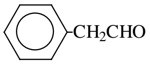
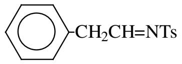
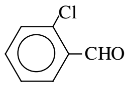
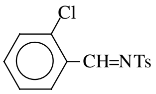
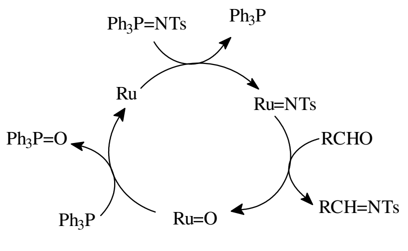
doi:10.1016/j.tetlet.2004.03.196

Table 1. Ruthenium catalyzed imidation of aldehydes by $Ph_3P{=}NTs$[a]

Entry	Aldehyde	Product	Reaction time (h)	Yield[b]
1			6	75
2			3.5	90
3			4.5	85
4			8	70
5			10	60
6			15	40
7			5.0	75

[a] Reaction conditions: aldehyde (1 mmol), $Ph_3P{=}NTs$ (1 mmol), $RuCl_2(Ph_3P)_3$ (0.05 mmol) at room temperature under a N_2 atmosphere.

[b] Isolated yields.



Scheme 2.

In summary, the present method describe a novel imido-transfer reaction of aldehydes with (*N*-tosylimino)triphenylphosphorane ($Ph_3P{=}NTs$) using $RuCl_2(PPh_3)_3$ as the catalyst under very mild conditions. The inexpensive and easy preparation of the reagent, mild reaction conditions and good yields of the products make this a facile method for the imidation of aldehydes.

Acknowledgements

We are thankful to the Director of IIP for his kind permission to publish these results. S. L. J. and V. B. S. are thankful to CSIR, New Delhi, for the award of a research fellowship.

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9. Typical experimental procedure: To a stirred suspension of benzaldehyde (1 mmol, 106 mg), $Ph_3P{=}NTs$ (1 mmol, 431 mg) in dry dichloromethane (5 mL) was added $RuCl_2(Ph_3P)_3$ (0.05 mmol, 5 mol %) under a nitrogen atmosphere at room temperature (20 °C). Stirring was continued for 6 h and, after completion, the solvent was evaporated under vacuum and the residue obtained was purified by passing through a silica gel column using hexane/ethyl acetate (9:1) as eluent. Evaporation of the solvent yielded the benzylidene *N*-(*p*-tolylsulfonyl)imine (194 mg, 75%), which was identified by comparing its physical and spectral data with those of an authentic sample.[10] The imidation of other aldehydes was similarly carried out and their reaction times and yields are given in the Table 1.
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