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Ruthenium catalyzed imido-transfer reactions of aldehydes: An easy access to *N*-sulfonyl aldimines under mild reaction conditions

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Abstract

(*N*-Tosylimino)triphenylphosphorane (Ph_3P=NTs) and [*N*-(*p*-toslylsulfonyl)imino] phenyliodinane (PhI=NTs) were found to be efficient imido-transfer reagents for imidation of aldehydes using [$RuCl_2(PPh_3)_3$] as the catalyst. A probable mechanism for this reaction is proposed.

Keywords: Imidation; Ruthenium; Aldehyde; Ph_3P=NTs; PhI=NTs

1. Introduction

The use of imido-metal complexes (M=NTs) formed in situ from metal complexes and nitrene precursors have become a powerful tool for the aziridination of alkenes, amidation of alkanes and allylic amination of alkenes [1–2]. In the recent years [*N*-(*p*-tolylsulphonyl)imino] phenyliodinane (PhI=NTs) [3] has come out to be a very convenient nitrene precursor and has been widely used for the aziridination of a variety of alkenes [4–9] and amination reactions [10–12] in the presence of several transition metal based catalysts. Recently, Che and co-workers [1] 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.

Imination of carbonyl compounds is an important synthetic transformation [13,14] 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 [15,16]. A variety of methods for the preparation of *N*-tosyl imines have been reported in Refs. [17,18] but most of these suffer from the drawbacks, such as the lower yields of the products, harsh reaction conditions like use of strong Lewis and Bronsted acids and longer reaction times. In our preliminary communication [19], we reported for the first time, the use of (*N*-tosylimino)triphenylphosphorane (Ph_3P=NTs) as an imido-transfer reagent for the imidation of various aldehydes using [$RuCl_2(PPh_3)_3$] as the catalyst (Scheme 1). Now we report details of this reaction and further application of [*N*-(*p*-toslylsulfonyl)imino] phenyliodinane (PhI=NTs) for imidation of various aldehydes using [$RuCl_2(PPh_3)_3$] as catalyst (Scheme 2).

2. Results and discussion

Equimolar quantities of Ph_3P=NTs and benaldehyde when reacted in dry dichloromethane in presence of catalytic amounts of [$RuCl_2(Ph_3P)_3$] at room temperature (20 °C) for 6 h, gave benylidine-*N*-(*p*-tolylsulfonyl) imine in 75% yield. The reaction was generalized by using various aldehydes and all the aldehydes were smoothly converted to their corresponding *N*-tosyl imines in good yields. The identities of the *N*-tosyl imines were established by comparing their physical and spectral data with those of authentic samples prepared by the literature procedures [20–24]. The results obtained are presented in Table 1 and show that while, aromatic aldehydes were found to be more reactive than

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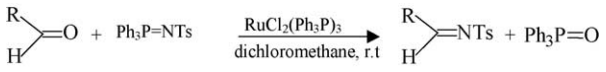
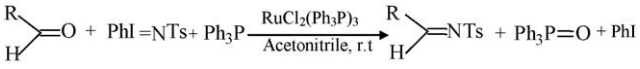


Scheme 1.

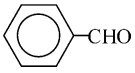
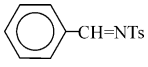
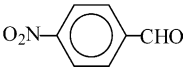
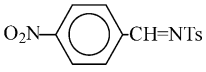
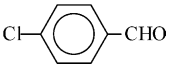
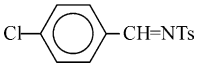
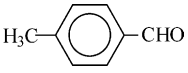
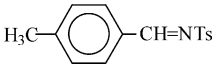
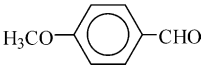
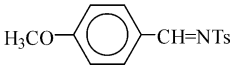
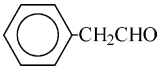
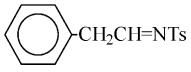
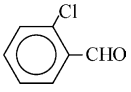
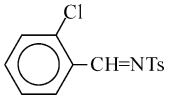


Scheme 2.

phenylacetaldehyde (Table 1, entry 6) amongst the various aromatic aldehydes studied those substituted with electron withdrawing groups were more reactive and required shorter reaction times. To evaluate the effect of catalyst blank experiment was carried out under similar reaction conditions without catalyst by employing 4-nitrobenzaldehyde as substrate. The reaction did not complete even after 12 h and the yield of 4-nitrobenylidine *N*-(*p*-tolylsulfonyl) imine was found to be very poor. The imino-transfer reaction of 4-nitrobenaldehyde was studied under usual reaction conditions using different solvents; these results are presented in Table 2. Among the different solvents like dichloromethane, acetonitrile, 1,2-dichloroethane and toluene studied, dichloromethane was found to be the best.

Further keeping in view the importance of [*N*-(*p*-toslylsulfonyl)imino] phenyliodinane (PhI=NTs) as emerging nitrene precursor we investigated for the first time its use as imido-transfer reagent for imidation of aldehydes. Imidation of a variety of aldehydes was carried out by reacting the aldehydes with PhI=NTs in presence of triphenylphosphine using 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 again like Ph_3P=NTs while aromatic aldehydes were found to be more reactive than phenylacetaldehyde (Table 1, entry 6), amongst the aromatic aldehydes studied those substituted with electron withdrawing groups (Table 1, entry 2, 3, 7) were more reactive and required lesser reaction times. The presence of triph-

Table 1
Ruthenium catalyzed imidation of aldehydes

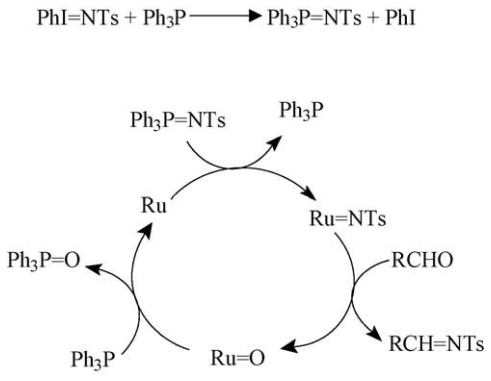
Entry	Aldehyde	Product	Method A		Method B	
			Reaction time (h)	Yield*	Reaction time (h)	Yield*
1			6	75	8	75
2			3.5	90	4.0	85
3			4.5	85	5.0	80
4			8	70	10	75
5			10	60	12	70
6			15	40	20	40
7			5.0	75	7.0	75

Method A: imidation with Ph_3=PNTs.
Method B: imidation with PhI=NTs.
* Isolated yields.

Table 2
Effect of solvent on imidation of aldehydes[a]

Entry	Substrate	Solvent	Method A		Method B	
			Reaction time (h)	Yield*	Reaction time (h)	Yield*
1	4-Nitrobenzaldehyde	Acetonitrile	4.5	75	4.0	80
2	4-Nitrobenzaldehyde	Dichloromethane	3.5	90	6.5	72
3	4-Nitrobenzaldehyde	Toluene	8.0	50	–	–
4	4-Nitrobenzaldehyde	Benzene	–	–	10.0	55
5	4-Nitrobenzaldehyde	Dichloroethane	5.0	82	6.0	70

Method A: imidation with Ph_3P=NTs.
Method B: imidation with PhI=NTs.
[a] Reaction conditions as mentioned in the text.
* Isolated yields.



Scheme 3.

enylphosphine was found to be essential and the reaction did not proceed in its absence. When the ruthenium catalyzed imidation of benzaldehyde was carried out using styrene as the reductant in place of triphenylphosphine, no imidation of benzaldehyde was observed and *N*-(*p*-tolylsulphonyl)-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 tris-(triphenylphosphine)ruthenium dichloride $[RuCl_2(PPh_3)_3]$ as catalyst and the yield of PhCH=NTs was found to be very poor indicating that copper complexes contrary to aziridination are very poor catalyst for the imidation of aldehydes. 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 case with copper-nitroids (Cu=NTs). To evaluate the effect of solvents, the imidation of 4-nitrobenzaldehyde was carried out using different solvents, such as acetonitrile, dichloromethane, 1,2-dichloromethane and benzene. Among the different solvents studied, acetonitrile was found to be the best reaction medium for this transformation. Results of these experiments are presented in Table 2. All these reactions were associated with the formation of *p*-toluenesulphonamide as a by-product and the presence of 5 Å molecular sieves in the reaction mixture showed significant decrease in *p*-toluenesulphonamide formation.

The similarities observed in the reactivity pattern and reaction rates for the imidation of various aldehydes while using Ph_3P=NTs and PhI=NTs as imido-transfer reagents, indicating the involvement of similar mechanistic pathways. Therefore, tentative mechanism for this reaction could be the formation of Ph_3P=NTs from Ph_3P and PhI=NTs [25] which, in turn give ruthenium-imido intermediate by its reaction with $[RuCl_2(PPh_3)_3]$. The imido transfer from ruthenium-imido intermediate to aldehyde yield *N*-tosyl imine as shown in Scheme 3. The observed fact that the imidation of aldehydes with PhI=NTs does not proceed without Ph_3P supports the formation of Ph_3P=NTs intermediate. The appearance of triphenylphosphine as indicated by TLC during the imidation of benzaldehyde with Ph_3P=NTs also supports the intermediacy of a ruthenium-imido complex.

3. Experimental

All the substrates used were commercially available and acetonitrile was distilled and dried over anhydrous CaH_2 before use. (*N*-Tosylimino)triphenylphosphorane (Ph_3P=NTs) was prepared by bromination of Ph_3P to obtain Ph_3PBr_2 followed by its reaction with *p*-toluenesulfonamide essentially following the procedure reported by Homer and Oediger [26]. The [*N*-(*p*-tolylsulphonyl)imino] phenyliodinane (PhI=NTs) [3] and $[RuCl_2(PPh_3)_3]$ [27] were prepared following the literature procedures. Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on Bruker 300 MHz and chemical shift values are recorded in δ units (parts per million) relative to Me_4Si as internal standard. IR spectra were recorded on a Perkin-Elmer 1760 X FTIR spectrometer in potassium bromide disc or neat thin film.

3.1. Typical experimental procedure for the imidation of benzaldehyde with PhI=NTs:

To a stirred suspension of benzaldehyde (1 mmol, 106 mg), PhI=NTs (1.5 mmol, 560 mg) and triphenylphosphine (1.2 mmol, 314 mg) in dry acetonitrile (5 ml) was added $[RuCl_2(PPh_3)_3]$ (0.05 mmol, 5 mol%) under nitrogen atmosphere at room temperature (20° C). Stirring was continued for 8 h (completion of the reaction as 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*-tolylsulphonyl)imine (194 mg, 75%) which was identified by comparing the physical and spectral data with those of authentic sample [21]. Similarly, the imidation of other aldehydes was carried out and their reaction times and yields are given in the Table.

3.2. Product identification

Benzylidine N-(p-tolylsulphonyl)imine (Table 1, entry 1): mp 107 °C (Ref. [20] 109), IR (KBr): 1650, 1570, 1380, 1320, 1160 (cm^{-1}); ^{1}H NMR ($CDCl_3$, δ): 2.46 (s, 3H), 7.36–7.96 (m, 9H), 9.05 (s, 1H).

4-Nitrobenzylidine N-(p-tolylsulfonyl)imine (Table 1, entry 2): mp 205–7 °C (Ref. [20] 206), IR (KBr) 1658, 1638, 1575, 1324, 1166 (cm^{-1}); ^{1}H NMR ($CDCl_3$, δ) 2.45 (s, 3H), 7.32–7.80 (m, 8H), 9.03 (s, 1H).

4-Chlorobenzylidine N-(p-tolylsulfonyl)imine (Table 1, entry 3): mp 175 °C (Ref. [20] 173), IR (KBr) 1650, 1580, 1320, 1162 (cm^{-1}); ^{1}H NMR ($CDCl_3$, δ) 2.42 (s, 3H), 7.30–7.85 (m, 8H), 9.02 (s, 1H).

4-Methylbenzylidine N-(p-tolylsulfonyl)imine (Table 1, entry 4): mp 114–5 °C (Ref. [21] 116), IR (KBr) 1652, 1575, 1322, 1160 (cm^{-1}); ^1H NMR ($CDCl_3$, δ) 2.42 (s, 3H), 2.38 (s, 3H), 7.28–7.85 (m, 8H), 9.01 (s, 1H).

4-Methoxybenzylidine N-(p-tolylsulfonyl)imine (Table 1, entry 5): mp 126–7 °C (Ref. [21] 128), IR (KBr) 1655, 1576, 1324, 1162 (cm^{-1}); ^1H NMR ($CDCl_3$, δ) 2.40 (s, 3H), 3.90 (s, 3H), 7.32–7.90 (m, 8H), 9.02 (s, 1H).

Phenylacetylidine N-(p-tolylsulfonyl)imine (Table 1, entry 6): mp 110 °C, IR (KBr) 1630, 1590, 1328, 1165 (cm^{-1}); ^1H NMR ($CDCl_3$, δ) 2.32 (s, 3H), 3.28 (d, 2H), 6.75–8.82 (m, 9H), 8.82 (t, 1H).

2-Chlorobenzylidine N-(p-tolylsulfonyl)imine (Table 1, entry 7): mp 125–7 °C (Ref. [22] 129), IR (KBr) 1650, 1572, 1320, 1162 (cm^{-1}); ^1H NMR ($CDCl_3$, δ) 2.46 (s, 3H), 7.32–7.90 (m, 8H), 8.90 (s, 1H).

4. Conclusion

In summary, the present method describes novel imido-transfer reactions of aldehydes with (*N*-tosylimino)triphenyl-phosphorane (Ph_3P=NTs) and [*N*-(*p*-toslylsulfonyl)imino] phenyliodinane (PhI=NTs) using [$RuCl_2(Ph_3P)_3$] as catalyst under very mild conditions. The inexpensive and easy preparation of the reagents, mild reaction conditions and goods yields of *N*-tosyl imines make these methods facile for the imidation of aldehydes.

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