A facile cleavage of the carbon-nitrogen bond of aromatic imines using acylation reagents in the presence of catalytic amounts of ytterbium triflate

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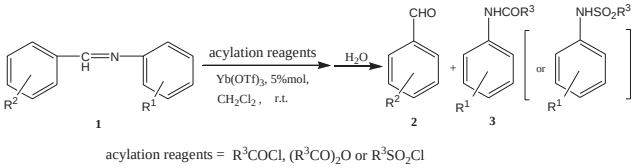
Catalytic amounts of ytterbium triflate were used to promote the cleavage of aromatic imines with acylation reagents, including acyl chlorides and anhydrides or sulfonyl chlorides, to obtain aldehydes and acyl amides or sulfonamides in high yields. Products of Friedel–Crafts acylation have not been detected.

Keywords: cleavage, imine, ytterbium triflate, acylation reagent

In recent decades, as the consciousness of protecting the environment has strengthened, methods which are cheap or are environmentally friendly are advocated. Ytterbium triflate, as an all-purpose strong Lewis acid, has been used in many organic reactions, such as Friedel–Crafts reactions, Diels–Alder reactions and Mannich-type reactions.[1] Its stability in water and its ease of recovery allows its re-use and promotes its environmental benefits.[2-4]

Imines, as Schiff bases, can cyclocondense with α-substituted acetyl chlorides or anhydrides to form lactams under basic conditions, such as in the presence of triethylamine or a similar base.[5-9]

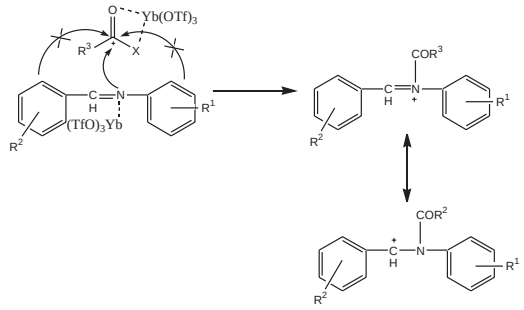
However, we found the imines can be cleaved easily by acylation reagents in the presence of catalytic amounts of $Yb(OTf)_3$ at room temperature to obtain the corresponding aldehyde and amide in high yields (Scheme 1). The results were summarised in Table 1.



Scheme 1

Results and discussion

From Table 1, it can be seen that the cleavage reaction between imines and acylation reagents can proceed smoothly at room temperature in the presence of $Yb(OTf)_3$ to obtain the corresponding products in high yields. Aldehydes and amides are obtained in almost equal yields from the reaction.



Scheme 2

Aliphatic acyl chlorides, such as acetyl chloride and butyryl chloride, can react with imines very quickly (Entries 1 and 3) in presence of $Yb(OTf)_3$, but aroyl chlorides usually need a longer time (Entries 4 and 6). Anhydrides react similarly to acyl chlorides, but more slowly (Entries 2 and 5).

Also, we found that 5%mol of $Yb(OTf)_3$ was enough to complete the reaction with high yields and an excess of the catalyst does not increase the yields perceptibly (Entry 12). We have also obtained the desired products by using anhydrous aluminium trichloride [$AlCl_3$] as the catalyst (Entry 11), but stoichiometric amounts of aluminium trichloride were needed to complete the reaction. Obviously, when aluminium trichloride was used as the catalyst, disposal of the aqueous aluminium salt is troublesome and wasteful. On the contrary, $Yb(OTf)_3$, as a strong Lewis acid, is stable in water and can be easily recovered and reused,[2-4] and only 0.05 equiv. was needed to complete the reaction (Entry 13).

In addition, Friedel–Crafts acylation does not take place under our experimental conditions even when an excess of the acylation reagent was used. We suggest that in the first set the

Table 1 Cleavage reaction of imines with acylation reagents catalyzed by ytterbium triflate[a]

Entry	Product **2** and **3**	R^1	R^2	Time/min	Acylation reagent	Yield[b]/% **2** and **3**
1	**2a, 3a**	*p*-OCH_3	H	20	CH_3COCl	94, 95
2	**2a, 3a**	*p*-OCH_3	H	45	$(CH_3CO)_2O$	92, 91
3	**2a, 3b**	*p*-OCH_3	H	20	*n*-C_3H_7COCl	94, 94
4	**2a, 3c**	*p*-OCH_3	H	60	C_6H_5COCl	89, 91
5	**2a, 3c**	*p*-OCH_3	H	120	$(C_6H_5CO)_2O$	92, 90
6	**2a, 3d**	*p*-OCH_3	H	60	*p*-$CH_3C_6H_4SO_2Cl$	91, 91
7	**2b, 3a**	*p*-OCH_3	*p*-CH_3	20	CH_3COCl	94, 94
8	**2b, 3b**	*p*-OCH_3	*p*-CH_3	45	*n*-C_3H_7COCl	93, 92
9	**2b, 3c**	*p*-OCH_3	*p*-CH_3	60	C_6H_5COCl	91, 93
10	**2b, 3d**	*p*-OCH_3	*p*-CH_3	60	*p*-$CH_3C_6H_4SO_2Cl$	91, 91
11	**2a, 3a**	*p*-OCH_3	H	120	CH_3COCl	85, 86[c]
12	**2a, 3a**	*p*-OCH_3	H	20	CH_3COCl	95, 95[d]
13	**2a, 3a**	*p*-OCH_3	H	20	CH_3COCl	94, 94[e]

[a]1 equiv. of acylation reagent and 5% mol of catalyst were used, based on imine. [b]Isolated yield based on imine.
[c]100% mol of $AlCl_3$ was used as the catalyst based on imine. [d]20% mol of $Yb(OTf)_3$ was used as the catalyst based on imine.
[e]Use of recovered $Yb(OTf)_3$.

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nitrogen atom would attack the carbonyl carbon to form amide (Scheme 2). In Scheme 2 we also postulate that the presence of the catalyst not only activates the acyl chloride but also the imine.

In conclusion, in the presence of catalytic amount of ytterbium triflate, imines can be easily cleaved to yield the corresponding aldehyde and amide in high yields. 5% mol of ytterbium triflate is enough to complete the reaction, and it can be recovered and reused easily.

Experimental

All reagents used are commercially available. ^{1}H NMR spectra were recorded on a Varian-400 MHz instrument using $CDCl_3$ as the solvent with TMS as an internal standard. IR spectra was recorded on a AVATAR-370 Infrared Spectrophotometer. Melting points were determined on a Digital Melting Point Apparatus WRS-1B and uncorrected. $Yb(OTf)_3$ was prepared from ytterbium oxide and trifluoromethanesulfonic acid in water according to the literature.[10]

General procedure: A dichloromethane solution (10ml) containing acyl chloride (1 mmol) and $Yb(OTf)_3$ (0.05 mmol) was treated with imine (1 mmol) at room temperature and the mixture was stirred for the given time (see Table 1) at room temperature, when the mixture was turned a deep yellow. It was treated with 5 ml water. Several minutes later, when the mixture was turned clear, the organic layer was isolated and the aqueous layer was extracted by dichloromethane (5 ml). The combined organic solution was dried (Na_2SO_4), concentrated in vacuum and then purified by TLC (cyclohexane / ethyl acetate = 4 / 1) to obtain the products.

2a: (Lit.[11]) ^{1}H NMR ($CDCl_3$) ppm δ: 7.48 (2H, m, ArH), 7.60 (1H, m, ArH), 7.87 (2H, m, ArH), 10.00 (1H, s, CHO); IR (cm^{-1}) 1704 (C=O).

2b: (Lit.[12]) ^{1}H NMR ($CDCl_3$) ppm δ: 2.45 (3H, s, CH_3), 7.30 (2H, d, *J*=8.2 Hz, ArH), 7.78 (2H, d, *J*=8.2 Hz, ArH), 10.00 (1H, s, CHO); IR (cm^{-1}) 1709 (C=O).

3a: M.p. 130.5–131.5°C (Lit.[13], 130–132°C) ^{1}H NMR ($CDCl_3$) ppm δ: 2.10 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 6.86(2H, d, *J* = 8.8 Hz, ArH), 7.40 (2H, d, *J* = 8.8 Hz, ArH), 7.88 (1H, s, NH); IR (cm^{-1}) 3300 (NH), 1671 (C=O).

3b: M.p. 86.8–88.2°C (Lit.[14], 86–89°C) ^{1}H NMR ($CDCl_3$) ppm δ: 1.23 (3H, t, *J*=7.2 Hz CH_3), 1.71 (2H, m, CH_2), 2.29 (2H, t, *J*=7.2 Hz, CH_2), 3.77 (3H, s, OCH_3), 6.83 (2H, d, *J* = 7.6 Hz, ArH), 7.42 (2H, d, *J* = 7.6 Hz, ArH), 7.76 (1H, s, NH); IR (cm^{-1}) 3280 (NH), 1652 (C=O).

3c: M.p. 155.4–157.0°C (Lit.[15], 156°C) ^{1}H NMR ($CDCl_3$) ppm δ: 3.81 (3H, s, OCH_3), 6.90 (2H, d, *J*=8.8 Hz, ArH), 7.85 (2H, d, *J*=8.8 Hz, ArH), 7.45–7.56 (5H, m, ArH), 7.80 (1H, s, NH); IR (cm^{-1}) 3331 (NH), 1650 (C=O).

3d: M.p. 114.1–115.6°C (Lit.[16], 114°C) ^{1}H NMR ($CDCl_3$) ppm δ: 2.30 (3H, s, CH_3), 3.77 (3H, s, OCH_3), 6.76 (2H, d, *J*=8.8 Hz, ArH), 7.05 (2H, d, *J*=8.0 Hz, ArH), 7.35 (2H, d, *J*=8.8 Hz, ArH), 7.60 (2H, d, *J*=8.0 Hz, ArH), 9.96 (1H, s, NH); IR (cm^{-1}) 3472 (NH), 1172 (SO_2).

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