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Polyhedron 25 (2006) 2525–2529
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Carbon–nitrogen bond cleavage by copper(II) complexes

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Received 20 January 2006; accepted 25 February 2006
Available online 22 March 2006

Abstract

N-benzoylimidazole reacts with copper(II) nitrate in the presence of different alcohols to give the benzoate of the corresponding alcohol and tetra(imidazole)copper(II) nitrate. The hydrolytic cleavage of *N*-benzoylimidazole in aqueous ethyleneglycol leads to the formation of imidazoliumbenzoate. Copper(II)nitrate trihydrate hydrolytically degrades *N*-benzoyl 3,5-dimethylpyrazole to form a copper complex in the form of an adduct having the composition *cis*-$(pz)_2Cu(OBz)_2 \cdot$ *trans*-$(pz)_2Cu(OBz)_2H_2O$ (where pz = 3,5-dimethylpyrazole and OBz = benzoate anion).

Keywords: *N*-benzoylimidazole; *N*-benzoyl 3,5-dimethylpyrazole; Copper(II)nitrate; Benzoylation; Catalysis; Copper(II)benzoate complex

1. Introduction

Protection of functional groups such as alcohol, amine and thiol is important in organic chemistry [1–3]. Various transition metal complexes catalyze such reactions [3]. Protection of a functional group may be done with an objective to facilitate further reactions on the parent substrate in the presence or absence of a transition metal catalyst. Thus, the stability of a functional group towards transition metal complexes is an important factor in the success of using them as a protected group. Hence, the development of new reagents for chemoselective protection and deprotection is a challenge [4–14]. Among such protection reactions, benzoylation is a fundamental reaction which can be performed under mild conditions [7,15–21]. Benzoylchloride is the most commonly used benzoylating reagent [7,15–21]. But, benzoylchloride is toxic and extra care is needed for performing benzoylation reactions with benzoylchloride. In addition to this, benzoylation of an alcohol by benzoylchloride leads to the formation of hydrochloric acid which can affect the benzoylation process and also can degrade an acid sensitive functional group. Thus, liberated acid in such a reaction needs to be scavenged by adding an amine [22–26]. Generally, tertiary amines are used for this purpose. Use of tertiary amine prevents formation of a stable *N*-benzoylated amine derivative, that can be formed as a side product if primary or secondary amines are used as the acid scavanger. Imidazole is observed to be an acid scavenger as well as a catalyst in esterification reactions [26,27]. Although, imidazole itself can react with benzoylchloride to form *N*-benzoylimidazole [28], catalytic reactions based on this as a reagent have not been studied in detail [26,27]. We discuss here the reactions of *N*-benzoylimidazole and *N*-benzoyl 3,5-dimethylpyrazole with copper(II) nitrate, and catalytic C–N bond cleavage reactions.

2. Experimental

2.1. Synthesis of *N*-benzoylimidazole (*I*)

To a solution of benzoylchloride (700 mg, 5 mmol) in dichloromethane (5 ml), triethylamine (606 mg, 6 mmol) was added. To this solution another solution of imidazole (340 mg) in dichloromethane (3 ml) was added dropwise at room temperature. The solution was stirred for 1.5 h. Dichloromethane (20 ml) was added to the reaction mixture

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doi:10.1016/j.poly.2006.02.019

followed by water (40 ml). The dichloromethane layer was separated and dried over anhydrous sodium sulfate. Distillation of dichloromethane extract gave *N*-benzoylimidazole (yield 90%) a colorless pasty liquid. IR (neat, cm^{-1}) 3150(s), 2843(s), 1711(s), 1603(s), 1552(s), 1383(s), 1327(m), 1327(m), 1276(s), 1178(m), 1071(s), 835(s), 717(s); ^1H NMR ($CDCl_3$) 7.84(s, 1H) 7.76–7.69(m, 1H), 7.56–7.53(m,2H), 7.46–7.42(m, 1H) 7.33–7.29(m, 2H), 6.918(s, 1H); ^{13}C NMR ($CDCl_3$) 137.48, 132.86, 131.12, 130.95, 129.06, 128.26, 127.65, 126.92; GC mass (*m/e*) 344 (for dimer), 277, 176, 116, 106, 78, 49, 38.

2.2. Synthesis of N-benzoyl 3,5-dimethylpyrazole (*II*)

To a solution of benzoylchloride (700 mg, 5 mmol) in dichloromethane (5 ml), triethylamine (606 mg, 6 mmol) was added. To this solution another solution of 3,5-dimethylpyrazole (480 mg, 5 mmol) in dichloromethane (6 ml) was added dropwise at room temperature. The solution was stirred for 3.5 h and to the reaction mixture dichloromethane (20 ml) was added, followed by addition of water (40 ml). The dichloromethane layer was separated by a separating funnel and dried over anhydrous sodium sulfate. Distillation of the dichloromethane extract gave the crude product. The crude product was washed with hexane (10 ml) to remove any hexane soluble impurity. The residue was filtered and the residue was found to be *N*-benzoyl 3,5-dimethylpyrazole (yield 92%). IR (neat, cm^{-1}) 3068(w), 2981(m), 2935(m), 1700(s), 1598(s), 1459(s), 1413(s), 1342(s), 1280(s), 1193(m), 1127(m), 1039(m), 978(s), 922(s), 804(m), 712(s). ^1H NMR ($CDCl_3$) 7.96–7.94(m, 2H), 7.58–7.40(m, 1H), 7.39–7.37(m, 2H), 6.0(s, 1H), 2.59(s, 3H), 2.20(s, 3H); ^{13}C NMR ($CDCl_3$): 167.82, 151.59, 144.59, 132.96, 131.96, 130.95, 127.40, 110.72, 14.17, 13.69. GC mass (*m/e*) 202, 172, 115, 105, 77, 59, 39.

2.3. Synthesis of imidazolium benzoate (*III*)

N-benzoylimidazole (176 mg 1 mmol) was dissolved in ethyleneglycol (1 ml). To this solution water (0.2 ml) was added. Standing for two days gave white crystals of imidazoliumbenzoate (60 mg). IR(KBr, cm^{-1}): 3401(bs), 3139(s), 2842(s), 1710(s), 1598(s), 1547(s), 1465(s), 1383(s), 1306(s), 1255(s), 1183(s), 1070(s), 1024(s), 896(s), 717(s). Elemental *Anal*. Calc. for $C_{10}H_{10}N_2O_2$: C, 63.13; H, 5.30; N, 14.73. Found: C, 63.58; H, 5.28; N, 14.26%. ^1H NMR ($CDCl_3$): 13.5(s,1H), 8.00–7.96(m, 1H), 7.67–7.65(m, 2H), 7.45–7.34(m,1H), 7.30–7.28(m, 2H), 7.06–7.01(m, 2H).

2.4. Synthesis of cis-$(pz)_2Cu(OBz)_2 \cdot$ trans-$(pz)_2Cu(OBz)_2H_2O$ (*B*)

To a solution of copper(II) nitrate trihydrate (242 mg, 1 mmol) in acetonitrile (3 ml) *N*-benzoyl 3,5-dimethylpyrazole (404 mg, 2 mmol) was added. The mixture was stirred to obtain a homogeneous solution. To this solution water (1 ml) was added. A blue crystalline precipitate appeared after 7 days (30 mg) on standing. The crystals were picked out and the structure was determined by X-ray diffraction. Elemental *Anal*. Calc. for $C_{48}H_{54}N_8O_9Cu_2$: C, 56.83; H, 5.37; N, 11.05. Found: C, 57.05; H, 5.56; N, 10.95; IR(KBr, cm^{-1}): 3206(m), 3145(m), 3047(w), 1628(s), 1582(m), 1531(s), 1403(s), 1296(m), 1183(w), 1070(w), 860(w), 804(w), 717(s). Crystal parameters of **B:** Monoclinic, space group *C2/c*, $a = 39.461(5)$, $b = 16.2272(17)$, $c = 11.6867(12)$ Å, $\alpha = 90.00°$, $\beta = 94.998(7)°$, $\gamma = 90.00°$, $V = 7455.1(15)$ Å^3, $Z = 4$, $T = 296$ K.

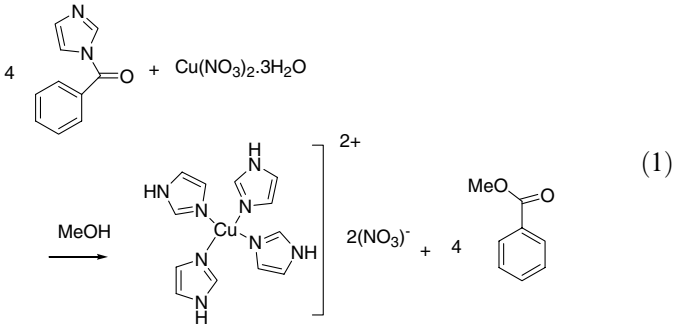
2.5. Copper(II) catalyzed benzoylation of alcohols by N-benzoylimidazole

In a typical experiment *N*-benzolylimidazole (115 mg, 1 mmol), copper(II) nitrate trihydrate (12 mg, 0.05 mmol) and nitric acid (0.01 M, 0.1 ml) were mixed together in methanol (2 ml) and stirred at room temperature. After 2 h of stirring, water (20 ml) was added to the reaction mixture and the organic products were extracted with dichloromethane (40 ml). The dichloromethane layer was separated using a separating funnel and dried over anhydrous sodium sulfate. Removal of dichloromethane from this extract under reduced pressure gave methylbenzoate as the only product. The compound was characterized by recording its ^1H NMR and IR spectra and comparing them with an authentic sample. Products from similar reactions with other alcohols were also confirmed by recording ^1H NMR and GC–MS spectra. For benzoylation of solid alcohols dry acetonitrile was used as the solvent. From a similar reaction of ethyleneglycol with *N*-benzoylimidazole under catalytic conditions only the mono-benzoylated ester was obtained. Spectral details of $C_6H_5COOCH_2CH_2OH$: IR (neat, cm^{-1}) 3416(bs), 1716(s), 1603(m), 1347(s), 1265(s), 1117(s), 707(s). ^1H NMR ($CDCl_3$): 8(m, 2H), 7.55(m, 1H), 7.4(m, 2H), 4.4(m, 2H), 3.9(m, 2H), 2.4(bs, exchangeable, 1H). GC–MS: (*m/e*), 167, 148, 135, 105, 77, 51.

3. Results and discussions

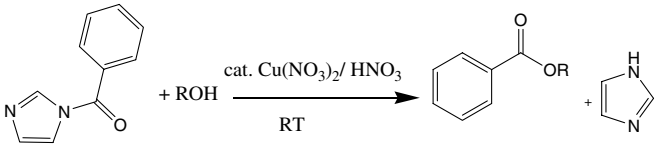
N-benzoylimidazole reacts with copper(II) nitrate trihydrate in methanol to form methylbenzoate and tetra-(imidazole)copper(II) nitrate (**A**) (Eq. (1)) under ambient conditions. Complex **A** has been characterized by determining its crystal structure by single crystal X-ray diffraction. The structure of this complex tallies with the one reported in the literature [28]. This reaction is a stoichiometric reaction. From this reaction, we could prepare the corresponding ester of methanol by using 1/4 molar ratio of copper(II) nitrate with respect to the *N*-benzoylimidazole. However, we had an important observation at this stage, if a drop of dilute nitric acid is added to the reaction mixture the esterification reaction worked catalytically. Inspired by this observation, we carried out a series of

benzoylation reactions by *N*-benzoylimidazole with different alcohols (Eq. (2)). The results showing the reaction time and yield obtained from these esterification reactions catalyzed by copper(II) under ambient conditions are listed in Table 1. In order to ascertain that the copper(II) nitrate, along with nitric acid, acts as a catalyst, we have carried out reactions under identical conditions without the catalyst and observed no significant reaction in this case. It is worth mentioning that the reaction of *N*-benzoylimidazole with nitric acid without copper(II) nitrate led to the formation of benzoic acid (1 ml, 0.1 M HNO_3, approximately 2 h for conversion of 1 mmol of *N*-benzoylimidazole). However, we used a lesser amount of the acid in our reactions; namely 0.1 ml of 0.01 M nitric acid for conversion of 1 mmol of *N*-benzoylimidazole to ester. These results clearly indicate that the catalytic ability of the copper(II) nitrate trihydrate is enhanced by the presence of the nitric acid. This probably happens because of protonation of the imidazole that is formed in the reaction by C–N bond cleavage. Imidazole in the absence of an acid can otherwise coordinate strongly to the copper(II) ion. This is further confirmed by adding nitric acid to tetra(imidazole)copper(II) nitrate in an independent experiment, which led to decomposition of this complex.



(1)

In addition to the primary alcohols, secondary alcohols such as isopropyl alcohol reacted very well to give the corresponding esters. The reaction does not work with tertiary alcohols such as *tert*-butanol. We also examined the reaction of *N*-benzoylimidazole with methanol in the presence of *tert*-butanol under catalytic conditions to ascertain if *tert*-butanol has a retarding effect on the rate. In this reaction only methylbenzoate was formed. It showed that *tert*-butanol does not hinder the benzolyation and also it does not itself give the corresponding ester under ambient conditions. Different allylic esters from allylic alcohols were also prepared by this copper(II) catalyzed reaction. However, in the case of decanol the reaction had to be carried out by suspending copper(II) nitrate trihydrate under heterogeneous conditions, as the later is not soluble in decanol. This solubility problem could be overcome by using complex **A** with very dilute nitric acid as a catalyst in acetonitrile as the solvent. Thus, the use of tetra(imidazole)copper(II) nitrate (**A**) as a catalyst instead of copper(II) nitrate trihydrate has an advantage as it minimizes the solubility problem in the case of long chain alcohols. Complex **A** is soluble in common solvents such as methanol, ethanol, acetonitrile; so the benzoylation reactions using complex **A** as a catalyst could be carried out in solvents other than the alcohols. The copper complex **A** does not have any water of crystallization, so the water content in the reaction is minimized and also the side reaction to give benzoic acid. Two illustrative examples using complex **A** as a catalyst are given in Table 1 (last two rows). Since our interest is on an alternative reagent for benzoylchloride, it is essential to know the stability of *N*-benzoylimidazole. *N*-benzoylimidazole itself gets hydrolytically cleaved in methanol/water mixture (1:1) in 24 h to give methylbenzoate and benzoic acid. However, it undergoes slow hydrolysis in ethyleneglycol. When *N*-benzoylimidazole was dissolved in ethyleneglycol containing traces of water; the water present in the ethyleneglycol reacted with it. After two days of reaction, we obtained white crystals of imidazoliumbenzoate from the reaction mixture. The role of ethyleneglycol in this salt formation reaction is presumably to provide a medium for the reaction to control the crystallization process. This fact is supported by the observation that an aqueous methanolic solution of *N*-benzoylimidazole on standing under ambient conditions gave benzoic acid as a crystalline product after five days. The reaction of ethyleneglycol with *N*-benzoylimidazole in the presence of a catalytic amount of copper(II) nitrate trihydrate and nitric acid gave the mono-benzolylated derivative of ethyleneglycol. It was earlier reported [18] that 1-(benzoyl)benzotriazole can be used for benzoylation of different diols in methylenechloride to give mono-benzoylated derivatives. These reactions were carried out in basic



R = Methyl, Ethyl, *iso*-propyl, benzyl, allyl, crotyl, propargyl etc.

(2)

Table 1
The results on copper(II) nitrate catalyzed benzoylation

Alcohol	Product	Time, yield (%)
CH_3OH	$C_6H_5COOCH_3$	2 h, 95
CH_3CH_2OH	$C_6H_5COOCH_2CH_3$	1.5 h, 86
$CH_3(CH_2)_3OH$	$C_6H_5COO(CH_2)_3CH_3$	2 h, 68
$(CH_3)_2CHOH$	$C_6H_5COOCH(CH_3)_2$	2 h, 94
$C_6H_5CH_2OH$	$C_6H_5COOCH_2C_6H_5$	2 h, 90
$CH_2{=}CHCH_2OH$	$C_6H_5COOCH_2CH{=}CH_2$	3 h, 56
$CH_3CH{=}CHCH_2OH$	$C_6H_5COOCH_2CH{=}CHCH_3$	2 h, 90
$CHCCH_2OH$	$C_6H_5COOCH_2CCH$	2 h, 86
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5COOCH_2CH{=}CHC_6H_5$	2 h, 76
Cyclo-$C_6H_{11}OH$	C_6H_5COO(cyclo-C_6H_{11})	2 h, trace
CH_2OHCH_2OH	$C_6H_5COOCH_2CH_2OH$	1 h, 92
$CH_3(CH_2)_7OH$	$C_6H_5COO(CH_2)_7CH_3$	3 h, trace
CH_3OH[a]	$C_6H_5COOCH_3$	1 h, 95
CH_3CH_2OH[a]	$C_6H_5COOCH_2CH_3$	1 h, 97

[a] With a catalytic amount of tetra(imidazole)copper(II) nitrate.

medium in the presence of triethylamine. Our copper catalyzed benzoylation reactions of *N*-benzoylimidazole with diols also gave only the mono-benzoylated product, but the difference is that the copper(II) catalyzed reactions were carried out under acidic conditions.

N-benzoyl 3,5-dimethylpyrazole on reaction with copper(II) nitrate trihydrate (2:1 molar ratio) in aqueous methanol at 25 °C for three days gave an interesting mixed copper(II) benzoate complex having the composition *cis*-$(pz)_2Cu(OBz)_2 \cdot$ *trans*-$(pz)_2Cu(OBz)_2H_2O$ (**B**) (where pz = 3,5-dimethylpyrazole and OBz = benzoate anion). The compound is structurally important (Fig. 1) as it has the distinction of having a unique lattice in which both *cis* and *trans* coordination of 3,5-dimethylpyrazole are present around two independent copper(II) centers. From this structure, the process can be understood to be co-crystallization of two inorganic neutral molecules in the form of an adduct. It is interesting to note that each of the two independent units, namely *cis*-$(pz)_2Cu(OBz)_2$ and *trans*-$(pz)_2Cu(OBz)_2H_2O$, is not held by any common weak interactions such as hydrogen-bonding, π-interactions or C–H···O interactions in the lattice but probably they are held by dipolar interactions due to a difference in the dipole moment of two the units. Such a difference in dipole moments is obvious from the orientation of the ligand as well as the coordination number of the two counterparts. The adduct (**B**) can also easily be prepared by the reaction of copper(II) acetate with benzoic acid in the presence of 3,5-dimethylpyrazole in methanol. However, reactions of copper(II) acetate with *o*-chlorobenzoic acid or *o*-nitrobenzoic acid and 3,5-dimethylpyrazole gives monomeric bis-3,5-dimethylpyrazole copper(II) *o*-chlorobenzoate or bis-3,5-dimethylpyrazole copper(II) *o*-nitrobenzoate respectively. Complex **B** has an interesting packing pattern, as shown in Fig. 2. It forms a parallel layered structure and the layers are formed by H-bonding interactions among the *cis*-$(pz)_2Cu(OBz)_2$ and *trans*-$(pz)_2Cu(OBz)_2H_2O$, independently. The layers are held by H-bonding interactions between the NH groups of the 3,5-dimethylpyrazole and the carboxylate oxygen atoms of each independent *cis*-$(pz)_2Cu(OBz)_2$ unit. In the *trans* counterpart, the H-bonding interactions occurs through the carboxyl oxygens with coordinated water and also through N–H···O interactions among carboxyl groups and N–H protons of the 2,3-dimethylpyrazole ligands.

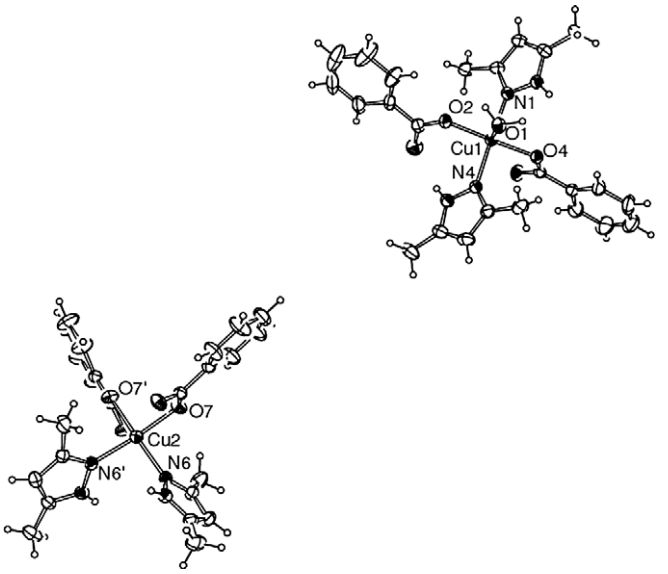


Fig. 1. Crystal structure of the adduct *cis*-$(pz)_2Cu(OBz)_2 \cdot$ *trans*-$(pz)_2Cu(OBz)_2H_2O$ (**B**).

All these results show that the formation of complex **A** is one of the driving forces for catalysis of *N*-benzoylimidazole, but in the case of *N*-benzoyl 3,5-dimethylpyrazole, such reactions gave a catalytically inactive complex **B**.

In conclusion we have shown that C–N bond cleavage by copper(II) complexes are not only useful for catalytic

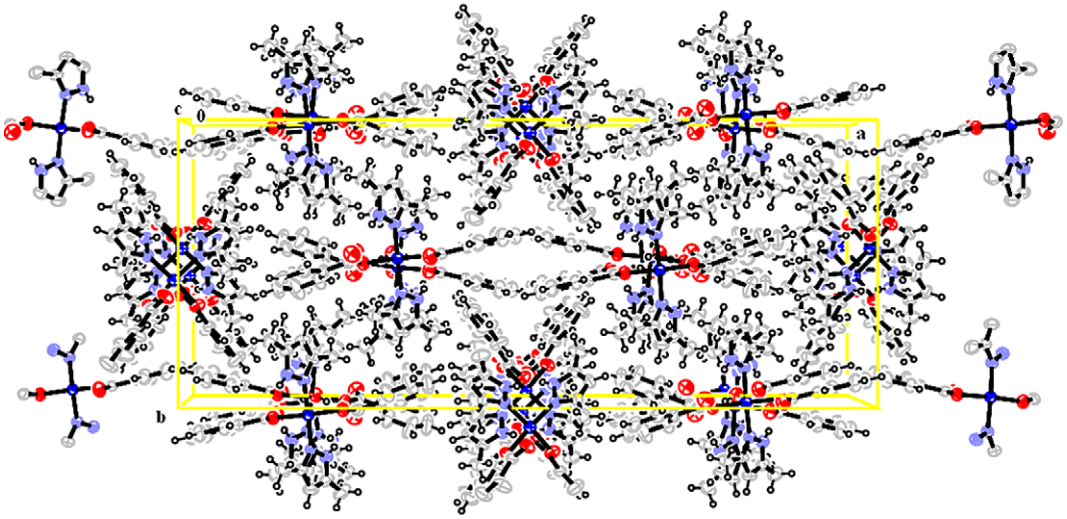


Fig. 2. The crystal packing in the adduct **B** viewed along crystallographic *c*-axis.

benzoylation reactions but also provide a method for the preparation of metal complexes.

Acknowledgments

The authors thank DST (New Delhi, India) for funding and the X-ray diffractometer facility. We thank Mr. R.J. Sarma for help with the crystallography.

Appendix A. Supplementary material

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 281721. Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk.

The GC mass of the *N*-benzoylimidazole and *N*-benzoyl 3,5-dimethylpyrazole are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.02.019

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