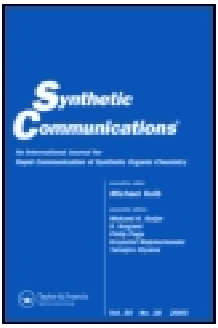

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Polyaniline-Anchored Metal Salts for Michael Reaction of α,β-Unsaturated Ketones

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Polyaniline-Anchored Metal Salts for Michael Reaction of α,β-Unsaturated Ketones

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Abstract: A catalyst consisting of polyaniline-anchored metal salts is used as a Lewis acid to promote the Michael reaction of α,β-unsaturated ketones. The reaction is performed efficiently with imidazole, acetyl acetone, and ethyl acetate as Michel donors and chalcones as the acceptors under ultrasound irradiation.

Keywords: Metal salts, Michael reaction, polyaniline, ultrasound

INTRODUCTION

Michael reaction of α,β-unsaturated ketones is an important process extensively used in synthetic organic chemistry.[1] The reaction works very well with different types of nucleophiles such as nitrogen,[2] sulfur,[3] oxygen,[4] and carbon,[5] leading to molecules with new bonds to β-carbon. When an amine is the nucleophile and α,β-unsaturated ester is the Michael acceptor, the product is a precursor of β-amino acid.[6]

Polyaniline and other polyamines are widely studied for their electrical conducting properties.[7] Polyaniline–hydrochloride can be easily polymerized to polyamine with ammonium peroxydisulfate to get solid polyaniline (PANI).

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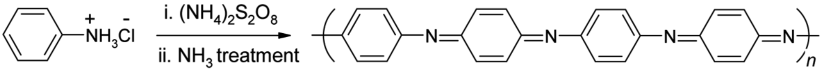


Polyaniline, PANI in one proposed form

The solid PANI, which has very low solubility in most of the organic solvents, is an ideal candidate for use as a solid support for the making heterogenous catalysts. The presence of several nitrogen atoms in PANI provide a perfect handle for the complexation with transition-metal ions, a prerequisite for a suitable catalyst support. There are a few reports of the use of polyaniline-anchored metal catalysts for catalytic reactions.[8] There are other applications such as polyaniline-supported MnO_2, which is used to decolorize dyes in industrial waste.[9]

RESULTS AND DISCUSSION

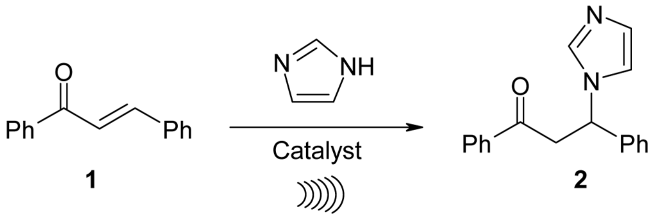
In this communication, we report our results in the use of PANI-supported metal catalysts for the Michael reaction on chalcones.[10] To test this reaction, a simple chalcone **1** was reacted with imidazole under different conditions. Polyaniline and its metal salts with $Co(OAc)_2$, $Cu(OAc)_2$, $FeCl_3$, and $MnCl_2$ were prepared by the reported method[8d] and tried as catalysts for this reaction. The results of the reaction run in an ultrasonic bath are summarized in Table 1. For this reaction, Cu–PANI as well as Montmorillonite K-10 clay[2b] were effective for this reaction.

A stronger Lewis acid, ferric chloride, was less effective for this reaction, probably because it binds too well with imidazole and does not smoothly effect the addition reaction.

The same reaction was then studied for reaction of **1** with acetyl acetone **4** and ethyl acetoacetate **5**, and results are summarized in Table 2.

The reactions of **4** or **5**, which possess acidic protons to give a stabilized carbon nucleophile for the catalytic Michael reaction with chalcone **1,** gave the products **6** or **7** respectively. The sample of only PANI without any metal ions does not give the reaction (entry 1, Table 2), and similarly the reaction without any catalyst in ultrasound did not work (entry 2). In this reaction, Fe–PANI was effective, whereas Cu–PANI did not work at all. The effect of ultrasound to enhance the reaction is clearly seen by comparison with the reaction conducted at room temperature at much longer time (entries 3 and 4).[11] Reaction of **3** with ethyl acetoacetate gave a nonseparable mixture of two isomers of **7**; its ratio was determined to be 88:12 based on H NMR (entry 6).

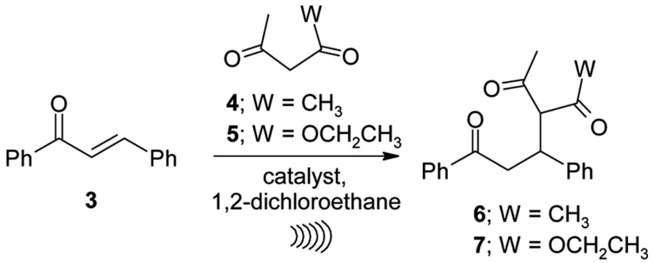
Table 1. Michael reaction of chalcone with imidazole



Entry	Catalyst/conditions	Isolated yield (%)
1	Co·PANI	No reaction
2	Cu·PANI	68
3	Fe·PANI	26
4	Mn·PANI	18
5	Montmorillonite K-10 (25% w/w)	60

Note. All the reactions were run in an ultrasonic bath for 2 h in 1,2-dichloroethane.

Table 2. Michael reaction of chalcone with diketone



Entry	Michael donor	Catalyst/conditions	Isolated yield (%)
1	Acetylacetone	PANI, ultrasound, 2 h	No reaction
2	Acetylacetone	No catalyst, ultrasound, 2 h	No reaction
3	Acetylacetone	Fe·PANI, ultrasound, 2 h	60
4	Acetylacetone	Fe·PANI, room temperature, 24 h	24
5	Acetylacetone	Cu·PANI, ultrasound, 2 h	No reaction
6	Ethyl acetoacetate	Fe·PANI, ultrasound, 2 h	53

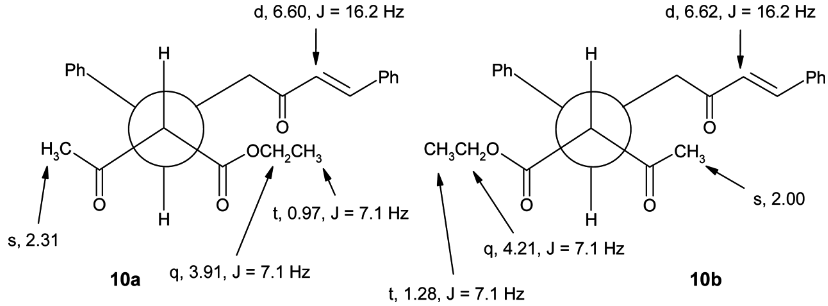
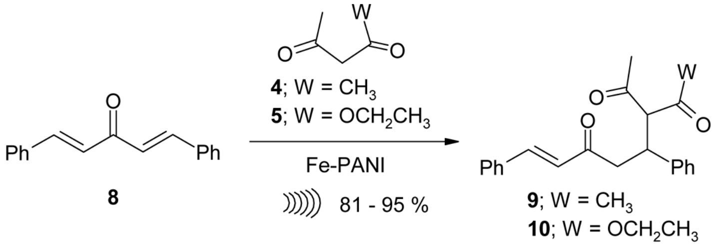


Figure 1. H NMR of **10a**, major (73), and **10b**, minor (27).

The Michael reaction of **4** and **5** was next studied with a *bis*-chalcone **8** with an aim to prepare a *bis*-Michael addition product. However, a large excess of **4** or **5** with Fe–PANI under ultrasound irradiation did not give the expected *bis* product; only single Michael addition took place, and products **9** and **10** were isolated in good yields.



The proton NMR of the product **10** indicated the presence of two isomers in the ratio of 73:27, which could not be purified by column chromatography. From the NMR pattern, the tentative assignment of the two isomers is shown in Figure 1.

The reaction of 1,5-diphenyl-1,4-pentadien-3-one **8** with 1,3-dicarbonyl compound in the presence of basic catalyst is reported[12] to give 1,1-disubstituted-2,6-diphenylcyclohexane-4-one, which was not observed in our reaction conditions.

EXPERIMENTAL

Polyaniline was prepared in aqueous acidic solution in the presence of ammonium persulfate with proper washing and drying.[8d] Its metal complexes were prepared by stirring the PANI with appropriate metal salt in acetic acid–acetonitrile (1:1) at room temperature for 36 h, following by proper washing with acetic acid, acetonitrile, and diethyl ether and drying at 80°C for 2 h. The chalcones were prepared from benzaldehyde–acetophenone for **1** and from acetone–acetophenone for **8** with NaOH solution.[13]

Standard Reaction Conditions

3-Acetyl-4,8-diphenyloct-7-en-2,6-dione (**9**)

A solution of 1,5-diphenyl-1,4-pentadien-3-one (0.2 g, 0.85 mmol), 2,4-pentadione (0.42 g, 4.0 mmol) , and catalyst Fe–PANI (0.1 g) was irradiated in an ultrasonic bath for 2 h. After the reaction was complete (as monitored by thin-layer chromatography), the mixture was diluted with diethyl ether and the catalyst was filtered. The solution was concentrated and purified by column chromatography over silica gel to afford pure product (0.27 g, 81%) as a white solid, mp = 139–41°C.

H NMR ($CDCl_3$, 400 MHz): δ 1.88 (s, 3H), 2.29 (s, 3H), 2.86–2.91 (dd, $J = 15.6$ & 4.4 Hz, 1H), 2.96–3.02 (dd, $J = 16.0$ & 8.8 Hz, 1H), 4.10–4.16 (m, 1H), 4.28–4.31 (d, $J = 10.8$ Hz, 1H), 6.54–6.58 (d, $J = 16.4$ Hz, 1H), 7.16–7.28 (m, 7H), 7.35–7.39 (m, 2H), 7.43–7.47 (m, 2H).

Data

3-Imidazol-1-Yl-1,3-diphenylpropan-1-one (**2**)

H NMR ($CDCl_3$, 400 MHz): δ 3.76–3.82 (dd, $J = 17.4$ & 5.8 Hz, 1H), 3.92–3.98 (dd, $J = 17.4$ & 7.9 Hz, 1H), 6.05–6.09 (dd, $J = 7.9$ & 5.8 Hz, 1H), 6.96 (m, 1H), 7.04 (m, 1H), 7.24–7.29 (m, 2H), 7.30–7.40 (m, 3H), 7.45–7.52 (m, 2H), 7.57–7.64 (m, 2H), 7.92–7.95 (m, 2H).

4-Acetyl-1,3-diphenylhexane-1,5-dione (**6**)

Mp = 146–47°C. H NMR ($CDCl_3$, 400 MHz): δ 1.88 (s, 3H), 2.28 (s, 3H), 3.16–3.21 (dd, $J = 16.3$ & 4.1 Hz, 1H), 3.29–3.35 (dd, $J = 16.3$ & 8.9 Hz, 1H), 4.21–4.25 (m, 1H), 4.31–4.33 (d, $J = 10.9$ Hz, 1H), 7.16–7.18 (m, 1H), 7.21–7.24 (m, 4H), 7.38–7.42 (m, 2H), 7.49–7.53 (m, 1H), 7.80–7.82 (m, 2H).

Ethyl(2-acetyl-5-oxo-3,5-diphenyl)pentanoate (**7**)

Mp 116–18°C. H NMR ($CDCl_3$, 400 MHz): δ 0.96 (t, $J = 7.05$ Hz, 3H of **7a**), 1.27 (t, $J = 7.05$ Hz, 3H of **7b**), 2.00 (s, 3H, of **7b**), 2.30 (s, 3H, of **7a**), 3.30–3.55 (m, 2H of **7a** & **7b**), 3.91 (overlapping q, 2H, **7a** & **7b**), 4.00–4.03 (m, 1H, of **7a** & **7b**), 4.14–4.19 (m, 1H, of **7a** & **7b**), 7.15–7.18 (m, 1H, of **7a** & **7b**), 7.21–7.24 (m, 4H, of **7a** & **7b**), 7.39–7.43 (m, 2H, of **7a** & **7b**), 7.50–7.54 (m, 1H, of **7a** & **7b**), 7.84–7.90 (m, 2H, of **7a** & **7b**).

Ethyl(2-acetyl-5-oxo-3,7-diphenyl)hept-6-enoate (**10**)

Mp = 125–28°C H NMR ($CDCl_3$, 400 MHz): δ 0.97 (t, $J = 7.1$ Hz, 3H, for **10a**), 1.27 (t, $J = 7.1$, 3H, for **10b**), 2.00 (s, 3H, for **10b**), 2.31 (s, 3H, for **10a**), 3.00–3.20 (m, 2H, for **10a** & **10b**), 3.91 (q, $J = 7.1$, 2H, for **10a**), 3.95–4.03 (m, 1H, for **10a** & **10b**), 4.05–4.16 (m, 1H, for **10a** & **10b**), 4.21 (q, $J = 7.1$ Hz, 2H, for **10b**), 6.60 (d, $J = 16.2$ Hz, 1H, for **10a**), 6.62 (d, $J = 16.2$ Hz, 1H, for **10b**), 7.14–7.21 (m, 1H, for **10a** & **10b**), **7.**22–7.29 (m, 4H, for **10a** & **10b**), 7.34–7.41 (m, 3H, for **10a** & **10b**), 7.42–7.52 (m, 3H, for **10a** & **10b**).

CONCLUSION

In this short communication, we report the application of PANI-supported metal salts for the Michael reactions on chalcones. These reactions are promoted by ultrasound irradiation to give good conversions in short and straightforward reaction conditions.

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REFERENCES

1. (a) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon: Oxford, 1992; (b) Sibi, M.; Manyem, S. Enantioselective conjugate additions. *Tetrahedron* **2000**, *56*, 8033–8061, and references cited therein.
2. Aza-Michael: (a) Kakumoto, K.; Kobayashi, S.; Sugiura, M. Transition metal salts-catalyzed aza-michael reactions of enones with carbamates. *Org. Lett.* **2002**, *4*, 1319–1322; (b) Shaikh, N. S.; Deshpande, V. H.; Bedekar, A. V. Clay-catalyzed chemoselective Michael type addition of aliphatic amines to α,β-ethylenic compounds. *Tetrahedron* **2001**, *57*, 9045–9048; (c) Yeom, C.-E.; Kim, M. J.; Kim, B. M. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)–promoted

efficient and versatile aza-Michael addition. *Tetrahedron* **2007**, *63*, 904–909, and references cited therein.

3. Oxy-Michael: (a) Greatrex, B. W.; Kimber, M. C.; Taylor, D. K.; Tiekink, E. R. T. A novel synthesis of functionalized tetrahydrofurans by an oxa-Michael/Michael cyclization of γ-hydroxyenones. *J. Org. Chem.* **2003**, *68*, 4239–4246; (b) Yamamoto, Y.; Momiyama, N.; Yamamoto, H. Enantioselective tandem *O*-nitroso aldol/Michael reaction. *J. Am. Chem. Soc.* **2004**, *126*, 5962–5963, and references cited therein.
4. Thia-Michael: (a) Li, H.; Wang, J.; Zu, L.; Wang, W. Organocatalytic asymmetric conjugate addition of thioacetic acid to β-nitrostyrenes. *Tetrahedron Lett.* **2006**, *47*, 2585–2589; (b) Chaudhuri, M. K.; Hussain, S. Boric acid–catalysed thia-Michael reactions in water or alcohols. *J. Mol. Cal. A: Chem.* **2007***, 269, 214–217, and references cited therein.*
5. Carbo-Michael: (a) Okino, T.; Hoashi, T.; Furukawa, T.; Xu, X.; Takemoto, Y. Enantio- and diastereoselective Michael reaction of 1,3-dicarbonyl compounds to nitroolefins catalyzed by a bifunctional thiourea. *J. Am. Chem. Soc.* **2005**, *127*, 119–125; (b) Liu, S.; Wolf, C. Asymmetric nitroaldol reaction catalyzed by a C_2-symmetric bisoxazolidine ligand. *Org. Lett.* **2008**, *10*, 1831–1834, and references cited therein.
6. (a) Rodriguez, J. Our recent contributions to the field of anionic domino transformations. *Synlett* **1999**, 505–518; (b) Simon, C.; Peyronel, J. F.; Rodriguez, J. A new multicomponent domino reaction of 1,3-dicarbonyl compounds: One-pot access to polycyclic *N/O-, N/S-*, and *N/N*-aminals. *Org. Lett.* **2001**, *3*, 2145–2148.
7. (a) Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. Polyaniline, a novel conducting polymer: Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385–2400; (b) MacDiarmid, A. G. "Synthetic Metals": A novel role for organic polymers (Nobel lecture). *Angew. Chem., Int. Ed.* **2001**, *40*, 2581–2590; (c) Stejskal, J.; Gilbert, R. G. Polyaniline: preparation of a conducting polymer. *Pure Appl. Chem.* **2002**, *74*, 857–867.
8. (a) Das, B. C.; Iqbal, J. Polyaniline-supported cobalt(II) catalyst: Oxidation of alkenes with molecular oxygen. *Tetrahedron Lett.* **1997**, *38*, 1235–1238; (b) Punniyamurthy, T.; Iqbal, J. Polyaniline supported cobalt(II)–salen catalyst: One-pot synthesis of b-phenylisoserine derivatives from cinnamoyl amides. *Tetrahedron Lett.* **1997**, *38*, 2903–2906; (c) Higuchi, M.; Ikeda, I.; Hirao, T. A novel synthetic metal catalytic system. *J. Org. Chem.* **1997**, *62*, 1072–1078; (d) Prabhakaran, E. N.; Iqbal, J. Polyaniline-supported cobalt catalyst: A three-component condensation route to β-amino acid derivatives. *J. Org. Chem.* **1999**, *64*, 3339–3341; (e) Nandy, J. P.; Prabhakaran, E. N.; Kiran Kumar, S.; Kunwar, A. C.; Iqbal, J. Reverse turn induced π-facial selectivity during polyaniline-supported cobalt(II)–salen–catalyzed aerobic epoxidation of N-cinnamoyl L-proline–derived peptides. *J. Org. Chem.* **2003**, *68*, 1679–1692; (f) Velusamy, S.; Ahamed, M.; Punniyamurthy, T. Novel polyaniline-supported molybdenum-catalyzed aerobic oxidation of alcohols to aldehydes and ketones. *Org. Lett.* **2004**, *6*, 4821–4824; (g) Lakshmi

Kantam, M.; Roy, M.; Roy, S.; Sreedhar, B.; Madhavendra, S. S.; Chaudary, B. M.; De, R. L. Polyaniline-supported palladium-catalyzed Suzuki–Miyaura cross coupling of bromo- and chloroarenes in water. *Tetrahedron* **2007**, *63*, 8002–8009.

9. Gemeay, A. H.; El-Sharkawy, R. G.; Mansour, I. A.; Zaki, A. B. Catalytic Activity Of Polyaniline/MnO_2 composites towards oxidative decolorization of organic dyes. *Appl. Catal. B: Environment* **2008**, *80*, 106–115.
10. (a) Lakshmi Kantam, M.; Roy, M.; Roy, S.; Subhas, M. S.; Sreedhar, B., Chaudary, B. M.; De, R. L. Polyaniline-supported indium chloride: A reusable catalyst for organic transformations in water. *J. Mol. Cat. A: Chem.* **2007**, *265*, 244–249; (b) Lakshmi Kantam, M.; Roy, M.; Roy, S.; Sreedhar, B.; De, R. L. Polyaniline-supported CuI: An efficient catalyst for C-N bond formation by N-arylation of N(H)-heterocycles and Benzyl Amines with aryl halides and arylboronic acids, and aza-Michael reactions of amines with activated alkenes. *Catal. Commun.* **2008**, *9*, 2226–2230.
11. Mason, T. J. *Sonochemistry*; Oxform Science Publications: New York, 1999.
12. (a) Bhaskar Reddy, D.; Padmavathi, V.; Muralidhar Reddy, M. Double Michael addition reactions of bischalcones. *Ind. J. Chem.* **1992**, *31B*, 407–410; (b) Li, J.-T.; Xu, W.-Z.; Chen, G.-F.; Li, T.-S. Synthesis of 1,1-disubstituted-2,6-diarlcyclohexane-4-ones catalyzed by KF/Al_2O_3 under ultrasound. *Ultrasound Sonochem.* **2005**, *12*, 473–476.
13. Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry,* 5th ed.; Pearson Education: New Delhi, 2006.