Pergamon

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Tetrahedron Letters 44 (2003) 9029–9032

TETRAHEDRON LETTERS

Microencapsulated $Cu(acac)_2$: a recoverable and reusable polymer-supported copper catalyst for aziridination of olefins

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Received 20 August 2003; revised 28 September 2003; accepted 29 September 2003

Abstract—Microencapsulated copper(II) acetylacetonate was prepared and used in the aziridination of alkenes employing [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrogen source. Microencapsulated copper(II) acetylacetonate [MC-$Cu(acac)_2$] catalyst was reused for several cycles with consistent activity.

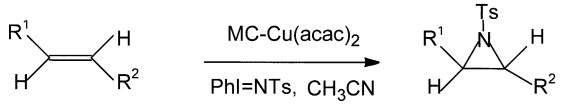
Aziridines are an important class of compounds in organic chemistry[1] and especially useful as intermediates for functional group modifications, efficient chiral auxiliaries[2] and ligands in asymmetric catalysis.[3] The synthesis of aziridines has therefore been a subject of considerable research interest over the last few years.

A single atom transfer to olefins is the shortest route to three-membered cyclic compounds. Catalytic addition of a carbene moiety to an imine results in the formation of an aziridine, but the yields are often low.[4] The transfer of a nitrogen atom onto an olefin offers an attractive synthesis of aziridines.

Evans et al. reported Cu(I) and Cu(II) salts[5] as the most effective and extensively used homogeneous catalysts for aziridination of olefins using [*N*-(*p*-tolylsulfonyl)imino] phenyl iodinane (PhI=NTs) as the nitrene donor. Taylor and co-workers[6,7] and Ando et al.[8] have reported copper-catalyzed aziridination of alkenes using chloramine-T as the source of the nitrene. Hutchings et al.[9,10] have, however, for the first time used heterogeneous copper-exchanged zeolite Y (CuHY) catalyst, using PhI=NTs as a nitrene donor for aziridination reactions. Later, a polymer-supported Ru-porphyrin catalyst,[11] a silica-supported polypyrazolylborate copper complex[12] and a polymer-supported manganese(II) complex[13] were also used for the aziridination of olefins by several other workers. However, these catalysts have some limitations such as tedious catalyst preparation, low yields of aziridines and long reaction times.

Immobilized catalysts have been of great interest due to several advantages, such as ease of product separation, isolation and reuse of the catalyst.[14] Recently, Kobayashi et al. have reported the use of microencapsulation as a technique for immobilizing metal complexes.[15–18] Microencapsulation is a rather new method for immobilizing catalysts onto polymers accomplished by physical envelopment by the polymers. This allows interactions between the π electrons of benzene rings of the polystyrene-based polymers and vacant orbitals of the catalyst (metal compounds) rendering the catalyst system more effective. This technique has been used in a variety of reactions such as [MC-$Sc(OTf)_3$] in aza Diels–Alder, Strecker, cyanation and alkylation,[19] Mannich-type and aldol reactions,[15] silylation of alcohols[20] and microencapsulated osmium tetroxide [MC-OsO_4] was used for dihydroxylation of olefins[16,21] and [MC-$Pd(PPh_3)$][18] for allylic substitution, Suzuki coupling and Mizoroki Heck reactions.

Considering the advantages of the microencapsulation technique, we have developed a MC-$Cu(acac)_2$ catalyst



Scheme 1.

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doi:10.1016/j.tetlet.2003.09.213

by immobilizing $Cu(acac)_2$ on polystyrene, and used this in the aziridination of alkenes. Incidentally, we have at our disposal a very clean and easy-to-operate method for the preparation of highly pure $Cu(acac)_2$[22] which facilitated the catalyst preparation. The preparation of the MC-$Cu(acac)_2$ is very simple and was accomplished following the Kobayashi protocol[15] using 1 g of polystyrene and 120 mg of $Cu(acac)_2$. Measurement of the mass increase of the resultant MC-$Cu(acac)_2$ indicates that 100 mg of $Cu(acac)_2$ is encapsulated, and the copper content is 0.38 mmol/g.

MC-$Cu(acac)_2$ catalyses the aziridination of a wide range of alkenes employing [*N*-(*p*-tolylsulfonyl)imino]-phenyl iodinane (PhI=NTs) as the nitrogen source (Scheme 1).

We have carried out aziridination of styrene using different nitrene donors such as chloramine-T, bromamine-T and PhI=NTs and the leaching of the metal for these nitrene donors was determined using an Atomic Absorption Spectrometer. The results are summarized in Table 1. The results confirmed that PhI=NTs is the preferred nitrene donor for our catalytic system.

A variety of alkenes were examined for this MC-$Cu(acac)_2$ catalyzed aziridination using PhI=NTs. Under the standardized conditions (MeCN, 5.6 mol% catalyst, 1 equiv. of PhI=NTs, 5 equiv. of olefin, 25°C), good yields of aziridines were obtained with both aromatic and aliphatic olefins. The results are summarized in Table 2. PhI=NTs, like its oxygen analogue PhI=O, is insoluble in a variety of solvents, including MeCN, dissolution of this reagent in the reaction indicates the completion of the reaction. It is clear from Table 2 that the catalyst gives the best results with phenyl substituted alkenes and moderate to good yields with simple olefins like *trans*-2-octene and 1-octene (entries 10 and 11, Table 2). All aliphatic olefins afforded good yields of aziridines without allylic insertion. The reaction of PhI=NTs with norbornene (entry 7, Table 2) occurs from the less hindered *exo* face of the bicyclic nucleus to provide the *exo* adduct in high yield and sterically hindered olefins like *trans*-stilbene (entry 6, Table 2) afforded the corresponding aziridines in good yields.

In order to confirm that this process is truly heterogeneous, the catalyst was removed after the reaction by filtration, fresh aliquots of reactants were added to the filtrate and the reaction was monitored by the dissolution of PhI=NTs. No product formation was observed. Further, the recovered catalyst could be reused for several cycles with consistent activity (Table 3).

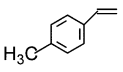
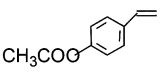
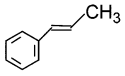
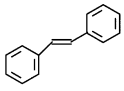
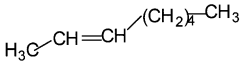
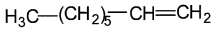
The present microencapsulated catalyst is more active than its homogeneous analogue, $Cu(acac)_2$ or a heterogeneous copper-exchanged zeolite Y (CuHY) catalyst (Table 2, entry 1). It is noteworthy that in earlier studies in the homogeneously catalyzed reaction,[4] the yield of aziridine decreased to 37% when the molar ratio of styrene: PhI=NTs was 1:1, due to the compet-

Table 1. Aziridination of styrene using various nitrene donors

Nitrene donor	Time (h)	Yield (%)[a]	Cu-Leaching (Wt%)
PhI=NTs	1	92	0.025
Chloramine-T	6	36	16.56
Bromamine-T	6	45	10.28

[a] Isolated yields.

Table 2. MC-$Cu(acac)_2$-catalyzed aziridination of alkenes[a]

Entry	Alkene	Time (h)	Yields (%)[b]
1		1	92, 90[c] 85[d] 95[e], 62[f]
2		1	85
3		1.5	76
4		1	82
5		2	80
6		2.5	74
7		2	88
8		2	52
9		1.5	70
10		3	45
11		6	35

[a] Unless otherwise specified reaction conditions were: MeCN, 25°C, alkene: PhI=NTs = 5:1.
[b] Isolated yield of aziridine based on PhI=NTs.
[c] With used catalyst.
[d] Styrene: PhI=NTs = 1:1 molar ratio.
[e] With 10 mol% of $Cu(acac)_2$.[5a]
[f] With 5 mol% of CuHY catalyst.[10]

Table 3. Recovery and reuse of the MC-$Cu(acac)_2$-catalyst for aziridination of alkenes[a]

Entry	Cycle no.	Isolated yield (%)
1	1	92
2	2	92
3	3	92
4	4	90
5	5	90

[a] MeCN, 25°C, alkene: PhI=NTs = 5:1.

ing breakdown of the PhI=NTs reagent to yield toluene-*p*-sulfonamide, whereas with our catalyst the yield is 85%. This is a particularly important observation because this procedure can be applied to the aziridination of expensive alkenes.

In conclusion, MC-$Cu(acac)_2$ is used as an effective catalyst for the aziridination of alkenes using PhI=NTs as the nitrene source with low catalyst loading. MC-$Cu(acac)_2$ catalyst can be reused for several cycles with consistent activity. The advantages of MC-$Cu(acac)_2$ are the ease of preparation and high activity.

Preparation of copper(II) acetylacetonate: Copper(II) acetate monohydrate (10 g, 50.09 mmol) was dissolved in 300 mL of water in a 500 mL beaker by warming at 60°C for 15 min. To the cooled solution, 20% aq. KOH was added slowly till the pH was raised to ca. 8 with constant stirring to precipitate the metal as its hydrated oxide. The metal hydroxide was washed with water till it was free of alkali by decantation, filtered and washed twice with cold water. Distilled acetylacetone (11.06 mL, 110 mmol) was added to the precipitate and mixed thoroughly with a glass rod. An exothermic reaction set in leading to the formation of blue shiny crystals of $Cu(acac)_2$. The mixture was allowed to stand at room temperature for 30 min and then placed in an ice-water bath for 15 min. The solid product was filtered through Whatmann No. 42 filter paper and dried in vacuo over fused $CaCl_2$ (yield: 12.49 g, 95%). The chemical analyses, IR and mass spectra of the compound match very well with those reported in literature.[23]

Preparation of the catalyst: Polystyrene (1.00 g, purchased from Aldrich) was dissolved at 40°C in cyclohexane (20 mL), and to this solution was added $Cu(acac)_2$ (0.12 g). This mixture was stirred for 1 h at this temperature and then slowly cooled to 0°C with vigorous stirring. The polystyrene solidified around the metal catalyst dispersed in the solution. Hexane (30 mL) was added to harden the capsule walls. The mixture was stirred at room temperature for 1 h, and the capsules were washed with acetonitrile several times to remove unencapsulated $Cu(acac)_2$ and then dried under vacuum.

General procedure: To acetonitrile (3 mL) were added MC-$Cu(acac)_2$ (0.15 g, 5.6 mol%), styrene (0.56 ml, 5 mmol) and PhI=NTs (0.372 g, 1 mmol) and the reaction mixture was stirred at room temperature. The reaction was monitored by disappearance of the PhI=NTs from the reaction mixture. After completion of the reaction, the catalyst was filtered and the filtrate concentrated and purified by column chromatography (hexane/ethyl acetate, 95/5, v/v) to afford pure product as white solid. Yield: 0.251 g, 92%. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 2H, $J=8.3$ Hz, Ar-H), 7.27 (m, 7H, Ar-H), 3.77 (dd, 1H, $J_{cis}=7.2$ Hz, $J_{trans}=4.5$ Hz, CHPh), 2.98 (d, 1H, $J=7.8$ Hz, *cis*-CH-aziridine) 2.43 (s, 3H, Ar-Me), 2.38 (d, 1H, $J=4.4$ Hz, *trans*-CH-aziridine).

Acknowledgements

B.K., V.N. and Y.H. thank the Council of Scientific and Industrial Research, India, for fellowships, S.K.D. is a IITG research fellow.

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