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Conjugate addition to diethyl azodicarboxylate under organic-perfluorinated biphasic homogeneous catalysis by nickel(II) species

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Abstract

The nickel(II) complex of the Schiff base of salicylaldehyde and 4-perfluorodecylaniline catalyzes the conjugate addition of β-diketones to electron-deficient substrates. Electrophilic amination with azodicarboxylate affords quaternary centers. The catalyst is recovered in solution and reutilized. Isolation of reaction products is very simple and does not require chromatography. © 2000 Elsevier Science Ltd. All rights reserved.

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Electrophilic amination is an important synthetic operation, in particular in the preparation of amino acids.[1] Conjugate addition to azodicarboxylates is one of the preferred methods of electrophilic amination. Transition metal-catalyzed conjugate additions are attractive since, avoiding the classical basic catalysis, secondary reactions are minimized.[2] Twenty years ago Nelson et al. reported the conjugate addition to electron-deficient compounds catalyzed by the Ni(II) complex of acetylacetone.[3,4] We found that the Ni(II) complex of salicylaldehyde is an even better catalyst since the complex of acetylacetone reacts with electrophiles, whereas the complex of salicylaldehyde does not.[5] However, after-work up salicyladehyde contaminates the final product, column chromatography being required. In the course of our research we needed an expeditious separation of the final products and we were attracted by the biphasic homogeneous catalysis with recovery of the catalyst in perfluorinated (or polyfluorinated) solvents.[6] Recovery of metal catalysts by this technique has been applied to metal-catalyzed cyclopropanations (Rh),[7] radical additions of trichloromethyl groups to olefins (Cu),[8] Heck and cross-coupling reaction (Pd),[9] allylation of nucleophiles (Tsuji–Trost reaction, Pd),[10] epoxidation of olefins (Mn, Ru),[11] hydroboration (Rh),[12] hydrogenation (Rh),[13] ethylene oligomerization (Ni),[14] and in reactions catalyzed by Lewis acids (Yb).[15]

Complex **3** was prepared by the sequence outlined in Scheme 1. Perfluoroalkylation of 4-iodoaniline by the general method of McLoughlin and Thrower[16] afforded **1**, which was converted into **3** by standard

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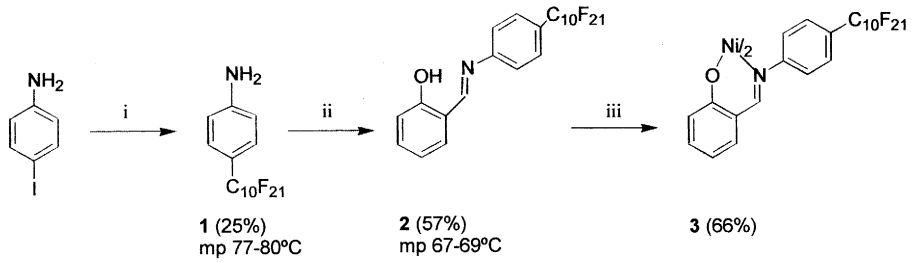
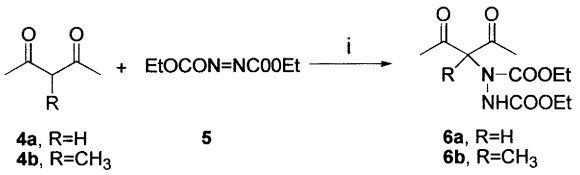
procedures. Reaction of acetylacetone (**4a**) with diethyl azodicarboxylate (**5**) was performed in a mixture of toluene and 1-bromoperfluorooctane (1:1) (Scheme 2). These solvents are miscible at 70–80°C, but form two layers at room temperature.[9a] The final product **6a** was recovered by precipitation from the toluene phase and was pure according to ^{1}H NMR and mp criteria,[5] further purification not being required.[16] The reaction was performed five times with the indicated yields. Clearly, four runs are at present the limit. The catalyst was also efficient in generating **6b**, possessing a quaternary center. Compound **6b** is an oil, and isolation from excess **4b** was achieved by distillation of **4b**. The residue was pure **6b** according to ^{1}H NMR and GC criteria. Again, the reaction was performed four times and only a noticeable drop in yield was observed in the fifth run. The lower yield observed in the first run is attributed to saturation of the prefluorinated phase with **6b**.[17]



Scheme 1. Preparation of **3**: (i) I-$C_{10}F_{21}$, Cu, DMSO, 130°C (Ref. 16); (ii) salicylaldehyde, toluene, azeotropic removal of water; (iii) $Ni(AcO)_2$, MeOH/water, 100°C



Yields for **6a** : 96, 96, 95, 77, 25 %
Yields for **6b** : 40, 92, 95, 80, 61 %

Scheme 2. Preparation of compounds **6**: toluene (15 mL)/BrC_8F_{17} (15 mL), **3** (2% molar, [**3**]=0.002 M), [**5**]=0.1 M, molar ratio **4**/**5**=2

In summary, nickel(II) complex **3** holds promise as an efficient catalyst in conjugate additions performed in neutral media, permitting easy isolation of final products.

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17. Experimental procedure: A solution of diketone **4** (6 mmol) in toluene (15 mL) was added to a stirred solution of **3** (0.08 g, 0.06 mmol (2%)) in 1-bromoperfluorooctane maintained at 60°C. The mixture was heated and stirred until one phase was formed. Then **5** (0.50 g, 3.0 mmol) was added, the mixture was refluxed for 3 days and then cooled at room temperature. The two phases were separated and the lower one was added to the second run. Compound **6a** (mp 122–125°C, lit.[5] mp 114–116°C) precipitated out from the toluene in the indicated yields (Scheme 2). For **6b** the toluene was evaporated and excess 3-methylacetylacetone was distilled off (bp 150°C/14 mmHg). The residue was pure **6b**. See Ref. 5 for spectral data of **6**.