A journey into amide and alkylamine synthesis from CO

Tawfiq Nasr Allah, T. Cantat

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AUTHORS
Tawfiq NASR ALLAH / CEA, NIMBE, CEA, CNRS-UMR 3685, GIF-SUR-YVETTE

PURPOSE OF THE ABSTRACT

Nitrogen containing molecules are essential for life. They are also key products in the chemical industry and are produced at the megaton scale. Among these compounds, amides and alkylamines are of particular importance. Amides are indeed among the most ubiquitous functions in living systems and form important materials (nylon, hydrogels, etc.), solvents, or pharmaceutics. An analysis carried out by the three leading pharmaceutical companies in 2006, revealed that amide bonds formation was used in the synthesis of 65% of the drugs candidates.[1]
Classically, amide compounds are synthesized from the reaction of an activated carboxylic acid derivative with an amine but traditional methods prove expensive with a poor atom economy.[2,3] An appealing alternative would consist in promoting the direct carbonylation of an amine with CO. During the last decade, a handful of catalysts were shown to facilitate the carbonylation of tertiary amines. However, they require harsh conditions (> 30 bar, > 190°C), and use of precious and/or toxic metal (palladium[4-6], rhodium[7,8] or cobalt[9,10]). In this context, we have designed the first system able to promote the carbonylation of amines to amides with iron catalysts. Low valent iron carbonyl complexes, in combination with a promotor (MeI) and a Lewis acid, favor the carbonylation of a variety of aromatic and aliphatic amines at low CO pressures (P < 8bar).

(Figure 1)

Ammonia's synthesis by the Haber-Bosch process has been a revolution ; yet, synthetic pathways to obtain alkyl and fatty amines, that are abundantly used remain challenging.[11] In particular, direct transformation of amines to heavier homologues by increasing the pendant alkyl chains is difficult, and we report an unprecedented catalytic method able to promote the selective homologation of methylamines (R2N-Me) to higher alkylamines R2N-(CH2)nMe with n=1-4, in presence of silanes as reductants.

(Figure 2)

FIGURES

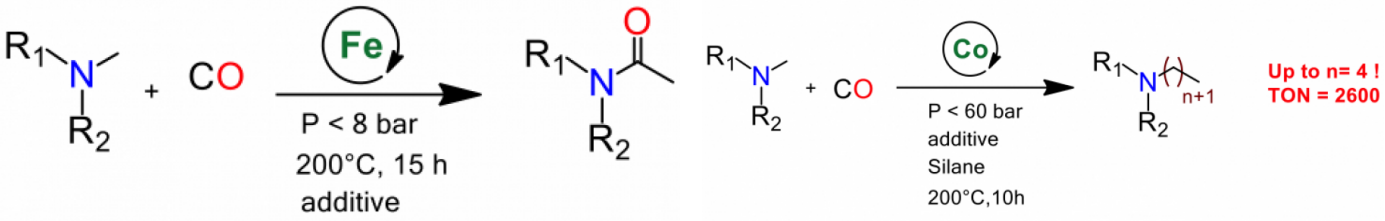

FIGURE 1

Carbonylation of amines.

Carbonylation of amines to amides with iron catalysts.

FIGURE 2

Homologation of methylamines.

Homologation of methylamines (R2N-Me) to higher alkylamines R2N-(CH2)nMe with n=1-4

KEYWORDS

CO | Catalysis | Homologation | Carbonylation

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