

Active-iron-promoted hydrodehalogenation of organic halides

Y. Moglie^a, F. Alonso^b, C. Vitale^a, M. Yus^{b,*}, G. Radivoy^a

^a *Instituto de Investigaciones en Química Orgánica (INIQO), Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina*

^b *Departamento de Química Orgánica, Facultad de Ciencias, and Instituto de Química Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain*

Received 16 May 2006; received in revised form 11 July 2006; accepted 12 July 2006

Available online 22 August 2006

Dedicated to Prof. Bruno Vuano on the occasion of his 68th birthday.

Abstract

Under very mild reaction conditions, the active-iron-based reducing system composed of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, an excess of lithium powder and a catalytic amount (5 mol%) of 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier, efficiently performed the hydrodehalogenation of alkyl and aryl halides in tetrahydrofuran at room temperature. The reaction of a series of alkyl and aryl chlorides, bromides, and iodides with this reducing combination led to the formation of the corresponding products resulting from a halogen/hydrogen exchange. Interestingly, the reducing system was efficient in the hydrodehalogenation of aryl fluorides and polychlorinated aromatics. The use of deuterium oxide instead of water in the iron salt allowed the preparation of the corresponding deuterated products. A reaction mechanism has been proposed on the basis of different experiments.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Active-iron; Hydrodehalogenation; Organic halides; Polychlorinated aromatics

1. Introduction

Organic halides remain important and versatile molecules with many applications in synthetic organic chemistry and in industrial chemical processes. Despite natural organohalogenes often possess an astonishing biological activity [1], many of synthetic origin are classified as high priority pollutants due to their adverse impact on the environment with persistent toxic effects (for reviews, see Ref. [2]). Therefore, efficient methods and techniques that allow their complete detoxification or transformation into less noxious chemicals are welcome. Several technologies have been developed in order to solve this environmental problem, i.e., incineration, pyrolysis, chemical [3] and biochemical degradation [4]. However, some of them lead to the formation of other halogenated pollutants or are methodologies not sufficiently developed.

On the other hand, chemical methods (for general methods reviews, see Ref. [5]) have demonstrated to be the most

effective and consequently the most studied ones. Among them, the reductive hydrodehalogenation of organic halides, a fundamental chemical transformation in organic synthesis (for a review on the metal-mediated hydrodehalogenation of organic halides, see Ref. [6(a)]; for a special issue on catalytic dehalogenation, see Ref. [6(b)]), represents an attractive alternative to the more noxious oxidative methods, allowing the conversion of halocompounds into more environmentally friendly and useful chemicals. Thus, catalytic hydrogenation (for a monograph, see Ref. [7(a)]; see also, for instance, Ref. [7(b)]), metal or low-valent metal compounds (for a review, see Ref. [8]), metal hydrides or complex metal hydrides (for monographs and reviews, see Refs. [9,10]), as well as some strong nucleophilic neutral or anionic species (for reviews, see Refs. [11,12]), are some of the general reagents and methods able to accomplish the above mentioned transformation. It is worthy of note that the use of zero-valent transition metals to degrade halogenated contaminants represents an active research area and one of the latest technologies for environmental remediation (see for instance, Ref. [13]). In this field, the use of iron metal prevails over other metals, mainly due to its virtually nil environmental impact, in fact there is no

* Corresponding author. Tel.: +34 965 903548; fax: +34 965 903549.

E-mail address: yus@ua.es (M. Yus).

exposure limit to humans, as stated by the OSHA (United States Occupational Safety and Health Administration). However, most of the studies carried out involving iron metal deal with a very specific type of substrates, mostly halomethanes, haloethanes, and haloethenes, whereas broader methodological studies covering the reactivity of the carbon–halogen bond (i.e. carbon hybridization or type of halogen) are very seldom [6(a)].

In recent years, we have studied new active-metal-based reducing systems, consisting of a mixture of hydrated chlorides of different transition metals ($\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), and lithium in the presence of a catalytic amount of an arene. The most studied $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ -Li-arene(cat.) system showed to be very effective in the reduction of a wide variety of functional groups (for a review, see Ref. [14]). The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -Li-arene(cat.) system was successfully applied to the reduction of carbonyl compounds and imines [15], as well as to that of sulfonates [16], whereas the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -Li-arene(cat.) exhibited a remarkable behaviour in the stereoselective reduction of cyclic ketones [17]. With regard to the hydrodehalogenation of organic halides, the active-nickel-based reducing system efficiently performed the reduction of alkyl and aryl halides (chlorides, bromides, and iodides), albeit fluorides remained unaltered [18]. The active-copper-based reducing system, in addition to the behaviour of the nickel-based analogue, showed to be effective in the hydrodehalogenation of both alkyl and aryl fluorides [19], its lower toxicity and commercial availability being additional advantages. Moreover, deuterium labeled compounds could be prepared in both cases when the deuterium oxide containing salts were used instead of the water-containing ones.

Our ongoing interest in the field above described, together with the intrinsic importance of a methodological comparative study about the reactivity of different transition metals, prompted us to explore new synthetic applications of these active-metal-based reducing systems, now focusing on iron, as a possible candidate to be used in the reduction of organic halocompounds.

We want to present herein our results on the study of the hydrodehalogenation of organic halides, under very mild reaction conditions, based on the use of active-iron, generated from commercially available iron(II) chloride tetrahydrate, lithium, and a catalytic amount of an arene (DTBB) as electron carrier.

2. Experimental

2.1. Materials

All moisture sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents used were treated prior to use by standard methods [20]. All starting materials were of the best available grade (Acros, Aldrich, Fluka, Merck) and were used without further purification. Commercially available iron(II) chloride tetrahydrate was used in the hydrodehalogenation reactions; its deuterated derivative $\text{FeCl}_2 \cdot 2\text{D}_2\text{O}$ was prepared by treating anhydrous iron(II)

chloride with an excess of deuterium oxide and then by heating in vacuo (*ca.* 0.5 Torr) at 80 °C in the short path for 1 h. Column chromatography was performed with Merck silica gel 60 (0.040–0.063 μm , 240–400 mesh). Thin layer chromatography (TLC) was performed on precoated silica gel plates (Merck 60, F254, 0.25 mm).

2.2. Instrumentation and analysis

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrophotometer using CDCl_3 as the solvent and tetramethylsilane (TMS) as internal reference. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. Infrared (FT-IR) spectra were obtained on a Nicolet-Nexus spectrophotometer. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-9A instrument equipped with a flame-ionisation detector and a 2 m column (1.5% OV17 9_A SUS Chrom 103 80/1000), using nitrogen as carrier gas.

2.3. Reduction of halogenated compounds using the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -Li-DTBB combination: general procedure

A solution of the halogenated compound (1.0 mmol) in THF (5 mL) was added to a mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (198 mg, 1 mmol) or its deuterated salt (166 mg, 1 mmol), lithium powder (56 mg, 8.0 mmol) and DTBB (27 mg, 0.1 mmol) in THF (5 mL) at room temperature under a nitrogen atmosphere. The reduction of 1-chloronaphthalene (Table 2, entry 4) was performed in the absence of an external arene as electron carrier, the substrate itself acting as an arene. The reaction mixture, which was initially dark green, changed to black, thus indicating the formation of activated iron(0). After total conversion of the starting material (GLC), the resulting suspension was diluted with diethyl ether (20 mL). Then, 10% HCl (20 mL) was added and the mixture stirred until transparency. The organic layer was washed with water (20 mL), dried over anhydrous sodium sulfate, and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate). For volatile products, the dried organic layer was analysed by GLC using toluene as an internal standard. The hydrodehalogenated products were fully characterised by comparison of their chromatographic and spectral data with those of the corresponding commercially available pure samples (*n*-nonane, *n*-dodecane, ethylbenzene, *tert*-butylbenzene, *iso*-butylbenzene, anisole, naphthalene, benzene, toluene, phenol, and biphenyl). *p*-Menthane [21], 4-deuteriotoluene [22], and 1-deuteriododecane [23] were characterised by comparison of their chromatographic and spectral data with those described in the literature.

3. Results and discussion

The hydrodehalogenation of a series of organic halides was successfully carried out using a mixture of commercially available iron(II) chloride tetrahydrate (1.0 mmol), an excess of

Download English Version:

<https://daneshyari.com/en/article/43940>

Download Persian Version:

<https://daneshyari.com/article/43940>

[Daneshyari.com](https://daneshyari.com)