

Selective, C,C-double bond reduction of α,β -unsaturated carbonyl compounds with cyclohexane using zeolites

Konstantin Yu. Koltunov, Stéphane Walspurger*, Jean Sommer

Laboratoire de physico-chimie des hydrocarbures, Université L. Pasteur, UMR 7513, Université L. Pasteur,
4 rue B. Pascal, 67000 Strasbourg, France

Received 26 July 2005; received in revised form 21 September 2005; accepted 23 September 2005
Available online 9 November 2005

Abstract

Selective ionic hydrogenation of α,β -unsaturated carbonyl compounds with alkanes (cyclohexane and others) was previously known to proceed only in superacidic conditions due to the necessity of dicationic, superelectrophilic activation of the enones. In present paper we disclose that H-form zeolites with acidity well below superacidity, are able however to induce the reduction of α,β -unsaturated carbonyl compounds with cyclohexane in strong analogy to the “parent”, superacid mediated reactions. The probable interpretation of these results in terms of highly electrophilic (superelectrophilic) intermediates on the solid is discussed.

© 2005 Elsevier B.V. All rights reserved.

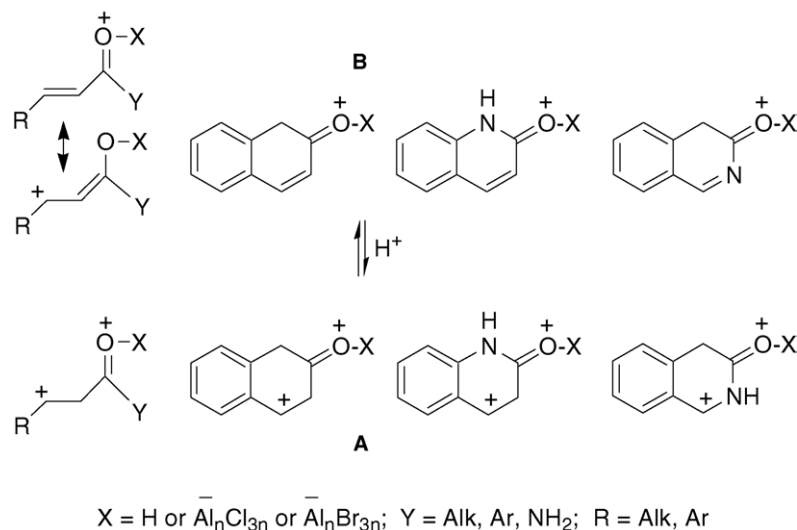
Keywords: Zeolites; Unsaturated compounds; Ionic hydrogenation; Superelectrophilic activation

1. Introduction

α,β -Unsaturated carbonyl compounds possess two sites which can undergo reduction: the carbonyl group and the adjacent C,C-double bond. While an abundant literature is available on the selective reduction of the carbonyl group, often achieved with relative ease, the selective hydrogenation of the double bond suffers from the lack of simple methods using practical chemicals. As a rare exception, 1,4-hydrometallation has been exhaustively studied and recent methods using metallic or organometallic hydrides are available [1]. In an effort to render this reaction more “eco-friendly” one can also quote catalytic hydrogenation over catalyst grafted on mesoporous material [2] as well as selective reduction using organocatalysis [3]. Among other practical applications, Jacquesy et al. have found 30 years ago that α,β -unsaturated ketones undergo selective, C,C-double bond ionic hydrogenation with alkanes (methylcyclopentane, cyclohexane) in superacid HF–SbF₅ ($H_o = -20$ to -25) [4]. As shown later, these and analogous reactions can be performed in milder but still superacidic media ($H_o \sim -18$

[4b,5]) using >2.5 molar excess of AlCl₃ or AlBr₃ promoted with traces of water (source of protonic acidity) [6]. Furthermore, relative 2-naphthol, dihydroxynaphthalenes, 2-quinolinol and 3-isoquinolinol exhibit similar reactivity in liquid superacid CF₃SO₃H–SbF₅ ($H_o \sim -18$), as well as in the presence of aluminum halides, giving practically important 2-tetralones and saturated heterocycles [7]. It is also recognized that the key intermediates of these reactions are superelectrophilic [8] dicationic species **A**, while monocationic forms **B** are inert (Scheme 1) [9]. This explains the necessity of superacidic conditions. However, from a synthetic point of view, to replace large excess of superacid by easily regenerable solid acid is obviously desirable for the development of this method of reduction, the interest of which resides in the exceptional selectivity and readily available source of hydride ions (alkane). In a similar context, we reported recently that H-zeolites, sulfated zirconia and Nafion, despite of comparatively low protonic acidity can be successfully applied in superelectrophilic activation to initiate some electrophilic aromatic substitution reactions, known previously to proceed only in superacidic conditions [10]. Worth to note, the effective excess of acidic sites appeared to be essential condition to provide these results. Inspired by this work, herein we disclose that H-form zeolites with acidity $H_o \sim -6$ [11], well below superacidity [4b], are able to induce the reduction

* Corresponding author. Tel.: +33 390241488; fax: +33 390241487.
E-mail address: wals@chimie.u-strasbg.fr (S. Walspurger).



Scheme 1. Dicationic species **A** and their monocationic precursors **B** as observed in liquid superacids [8].

of α,β -unsaturated carbonyl compounds with cyclohexane in strong analogy to “parent”, superacid mediated reactions.

2. Experimental

Zeolite USY (Si/Al=2.5, CBV500, Zeolyst International) in NH_4^+ form was activated at 550°C overnight under air. For quantitative estimation of Bronsted acid sites, see [12]. The starting compounds **1a–d** and **3a–c** are purchased. Amides **1e–f** are obtained as previously [6b]. All products are known compounds and their analytical data are convincing with those previously reported [6,7].

2.1. Typical procedure

2a: The activated zeolite (0.8 g, ~ 3.7 mmol protonic sites), compound **1a** (0.035 g, 0.24 mmol) and cyclohexane (4 ml) were loaded in 15 ml pressure tube. The resulting suspension was magnetically stirred at 130°C for 6 h. After cooling, water (4 ml) was introduced to the reaction mixture followed by continuous solid–liquid extractions with ether. The combined organic phase was dried (Na_2SO_4) and concentrated to provide the residue (0.031 g), which was analysed by NMR to give the conversion yield of **2a** stated in Table 1. The subsequent chromatographic purification (silica gel, benzene/acetone) gave **2a** (0.025 g, 70%) as individual product. ^1H NMR (300 MHz, CDCl_3): δ = 2.14 (s, 3H), 2.76 (t, 2H), 2.89 (t, 2H), 7.15–7.3 (m, 5H) [13]; ^{13}C NMR (75 MHz, CDCl_3): δ = 29.7, 30.1, 45.2, 126.1, 128.3, 128.5, 140.4, 208 [13].

The catalyst can be regenerated by filtration from the aqueous phase followed by dryness and calcination at 500°C without loss of activity.

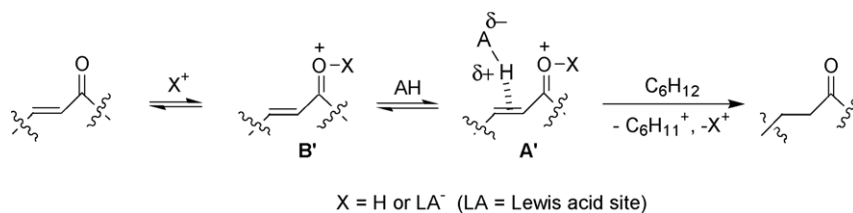
3. Results and discussion

First, the reactivity of model ketones **1a–c** was investigated. Their treatment with cyclohexane in the presence of HUSY-

zeolite afforded the saturated derivatives **2a–c** (Table 1, entries 1–3). The reaction required 130°C providing ~ 15 molar excess of acidic sites to be carried out in appropriate time, for several hours. Decreasing of the amount of acid slowed significantly the reaction (Table 1, entry 1). That is in accord with our previous observations [10]. Amides **1d–f** also underwent the reaction under similar conditions to give **2d–f** (Table 1, entries 4–6). What is remarkable, the HUSY mediated reduction of compounds **1a–f** generally appeared even more successful than that in superacidic media. On the other hand, the reaction of 2-naphthol (**3a**) as well as 2-quinolinol (**3b**) is notably less efficient, even after promotion by preliminary saturation of the reaction mixture with gaseous HCl (Table 1, entries 7 and 8). The negligible yield of products **4a** and **4b** (<20%) is in accord with relatively poor reactivity of **3a** and **3b** in the presence of aluminum halides [7], most probably due to reversibility of these reactions (which is already known for superacid mediated reactions of **3a** and **3b** with benzene [7d,14]). Compound **4a**, for example, gives **3a** in $\sim 30\%$ yield in the presence of HUSY (15 equiv. of acidic sites) and cyclohexane over 20 h at 130°C , while no reaction occurs when CCl_4 was used instead of cyclohexane, considered as a source of $\text{C}_6\text{H}_{11}^+$. This demonstrates some limitations of the ionic reduction using zeolites, which can be related to the elevated temperature conditions along with decreased concentration of reactive electrophiles, shifting the equilibrium to starting compounds.

It should be also noted, that regioselectivity of reduction of **3b** on HUSY is the same as in the presence of AlCl_3 , whereas in the presence of the protonic superacid, $\text{CF}_3\text{SO}_3\text{H}-\text{SbF}_5$ reduction occurs on the carbocyclic ring [7d]. That may be due to a strong involvement of Lewis acid sites in the activation on zeolite, as suggested previously [10].

Isoquinolinol **3c**, which is rather reactive towards cyclohexane in superacidic conditions [7c] appeared to be inert in the presence of HUSY (Table 1, entry 9). Moreover, at similar conditions **3c** does not react with (more reactive [7c]) benzene. Presently we cannot explain this result, which however seems



Scheme 2. Mechanistic proposal.

zeolite structure has been investigated recently by Tuma and Sauer [18].

In this connection it should be stressed, that the suggested mechanism cannot be supported by direct spectroscopic observation of protosolvated ions A' due to both their short life time and low concentration. Real dications such as A (Scheme 1) could only be observed as long living species in extremely acidic HF(HSO₃F)–SbF₅–SOCIF systems at –80 to –40 °C [9]. Nevertheless, the scope of presently available results including the data for superacid mediated reactions as well as the data from [10] suggests the involvement of intermediates A' as the best rationale of the found reactivity.

4. Conclusions

In conclusion, we have shown that a variety of α,β -unsaturated carbonyl compounds can be regioselectively reduced with cyclohexane in the presence of a solid acid, HUSY-zeolite. That presents a new remarkable example of the unusual catalytic ability of the solid acid which, despite of comparatively low protonic acidity is able to perform reactions only expected to occur under superacidic conditions.

Acknowledgements

Financial support of the work by the Loker Hydrocarbon Institute, U.S.C., Los-Angeles, and the “CNRS” is gratefully acknowledged.

References

- [1] (a) T. Kawakami, M. Miyatake, I. Shibata, A. Baba, *J. Org. Chem.* 61 (1996) 376, and references therein;
(b) L. Moisan, C. Hardouin, B. Rousseau, E. Doris, *Tetrahedron Lett.* 43 (2002) 2013;
(c) H.Y. Lee, M. An, *Tetrahedron Lett.* 44 (2003) 2775.
- [2] C. Simons, U. Hanefeld, I.W.C.E. Arends, R.A. Sheldon, T. Maschmeyer, *Chem. Eur. J.* 10 (2004) 5829.
- [3] J.W. Yang, M.T. Hechavarria Fonseca, B. List, *Angew. Chem. Int. Ed.* 43 (2004) 6660.
- [4] (a) J.M. Coustard, M.H. Douteau, J.C. Jacquesy, R. Jacquesy, *Tetrahedron Lett.* 25 (1975) 2029;
(b) G.A. Olah, G.K.S. Prakash, J. Sommer, *Superacids*, Wiley, New York, 1985.
- [5] (a) T. Xu, D.H. Barich, P.D. Torres, J.F. Haw, *J. Am. Chem. Soc.* 119 (1997) 406;
(b) G.P. Smith, A.S. Dworkin, R.M. Pagni, S.P. Zingg, *J. Am. Chem. Soc.* 111 (1989) 5075, and references cited.
- [6] (a) K.Yu. Koltunov, I.B. Repinskaya, G.I. Borodkin, *Russ. J. Org. Chem.* 37 (2001) 1534;
(b) K.Yu. Koltunov, S. Walspurger, J. Sommer, *Eur. J. Org. Chem.* 19 (2004) 4039.
- [7] (a) K.Yu. Koltunov, L.A. Ostashevskaya, I.B. Repinskaya, *Russ. J. Org. Chem.* 34 (1998) 1796;
(b) L.A. Ostashevskaya, K.Yu. Koltunov, I.B. Repinskaya, *Russ. J. Org. Chem.* 36 (2000) 1474;
(c) K.Yu. Koltunov, G.K.S. Prakash, G. Rasul, G.A. Olah, *J. Org. Chem.* 67 (2002) 8943;
(d) K.Yu. Koltunov, G.K.S. Prakash, G. Rasul, G.A. Olah, *Heterocycles* 62 (2004) 757.
- [8] (a) G.A. Olah, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 767;
(b) V.G. Nenajdenko, N.E. Shevchenko, E.S. Balenkova, I.V. Alabugin, *Chem. Rev.* 103 (2003) 229;
(c) G.A. Olah, D.A. Klumpp, *Acc. Chem. Res.* 37 (2004) 211.
- [9] For generation of some long-living dications A (X=H) in superacids and/or theoretical estimation of their electrophilicity, see:
(a) I.B. Repinskaya, K. Yu. Koltunov, M.M. Shakirov, V.A. Koptyug, *J. Org. Chem. USSR* 28 (1992) 785;
(b) K.Yu. Koltunov, I.B. Repinskaya, *Russ. J. Org. Chem.* 30 (1994) 97;
(c) K.Yu. Koltunov, G.K.S. Prakash, G. Rasul, G.A. Olah, *J. Org. Chem.* 67 (2002) 4330, and references 6 and 7c–d.
- [10] K.Yu. Koltunov, S. Walspurger, J. Sommer, *Chem. Commun.* 15 (2004) 1754.
- [11] J.F. Haw, *Phys. Chem. Chem. Phys.* 4 (2002) 5431, and references cited.
- [12] B. Louis, S. Walspurger, J. Sommer, *Catal. Lett.* 93 (2004) 81.
- [13] R. Akiyama, S. Kobayashi, *J. Am. Chem. Soc.* 125 (2003) 3412.
- [14] K.Yu. Koltunov, I.B. Repinskaya, M.M. Shakirov, L.N. Shchegoleva, *Russ. J. Org. Chem.* 30 (1994) 88.
- [15] (a) D.A. Klumpp, S. Lau, *J. Org. Chem.* 64 (1999) 7309;
(b) K.Yu. Koltunov, S. Walspurger, J. Sommer, *Catal. Lett.* 98 (2004) 89.
- [16] T. Xu, N. Kob, R.S. Drago, J.B. Nicholas, J.F. Haw, *J. Am. Chem. Soc.* 119 (1997) 12231, and references cited.
- [17] (a) A. Corma, *J. Catal.* 216 (2003) 298;
(b) E.G. Derouane, *J. Mol. Catal. A* 134 (1998) 29.
- [18] C. Tuma, J. Sauer, *Angew. Chem. Int. Ed. Engl.* 44 (2005) 4769.