

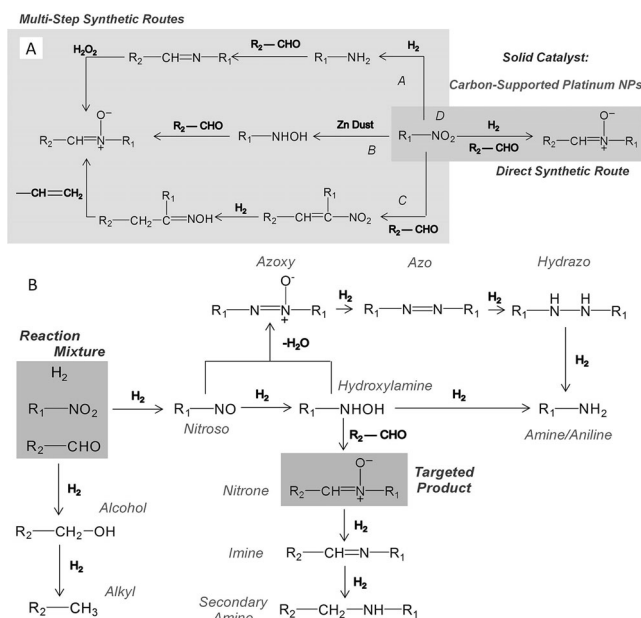
Selective Reductive Coupling of Nitro Compounds with Aldehydes to Nitrones in H₂ Using Carbon-Supported and -Decorated Platinum Nanoparticles**

Larisha Cisneros, Pedro Serna,* and Avelino Corma*

Abstract: Nitrones were synthesized in high yields directly from nitro compounds, aldehydes, and H₂ using carbon-decorated platinum nanoparticles. The high selectivity for nitrone synthesis contrasts that of common supported metal catalysts and corresponds to an increase from roughly 6 to 97 %. The catalytic performance is tuned by precise control of the structure of the active sites and the characteristics of the support.

Nitrones are important organic building blocks with applications as radical spin-traps,^[1] antioxidants,^[2] enzymes inhibitors,^[3] and precursors of a number of specialty nitrogen-containing derivatives such as isoxazolidines, isoxazolines, and β-amino alcohols.^[4] β-Lactams, which are among the most commonly prescribed drugs in the world, can be obtained, for example, from nitrones through 1,3-dipolar cycloaddition with alkynes,^[5] and important γ-amino ester derivatives can be synthesized by the addition of nitrones to α,β-unsaturated esters.^[6] The synthetic value of nitrones is prominent and new reactions are continuously emerging, for example, for the preparation of novel molecules that incorporate chiral centers by means of stereocontrolled nucleophilic additions.^[7a–g]

Typically, nitrones are synthesized by one of the following routes (Scheme 1A):^[8] a) oxidation of secondary amines,^[9] hydroxylamines,^[10] or imines;^[11] b) condensation of carbonyl compounds with hydroxylamines;^[12] and c) N-alkylation of oximes.^[13] Hydroxylamines can be synthesized by partial hydrogenation of nitro compounds (Scheme 1A, route b). The low stability of the NHOH group limits, however, the class of reducing agents that can be employed. Whereas stoichiometric reducing agents such as Zn dust afford the hydroxylamine intermediate in high yields,^[14] solid metal catalysts used with H₂, industrially preferable, are inefficient



Scheme 1. A) Some representative routes for the synthesis of nitrones. Common protocols require several reaction steps and the use of stoichiometric reducing agents. Carbon-supported Pt nanoparticles form the nitrone selectively directly from an aldehyde, a nitro compound, and H₂. B) Typical reactions in mixtures of H₂ and nitro and carbonyl compounds.

due to complete reduction of the NO₂ group, and/or the formation of azo, azoxy, or hydrazo intermediates.^[15] Further inconveniences associated with hydroxylamines are the fact that cannot be stored, are potentially explosive,^[15] and have only limited commercial availability.

Oximes, on the other hand, are often synthesized by condensation of hydroxylamine and carbonyl compounds. Alternatively, oximes can be obtained by hydrogenation of α,β-unsaturated nitro compounds, which requires a catalyst that prevents the reduction of the C=C bond. Gold nanoparticles supported on TiO₂ exemplify such a catalyst, facilitating the formation of the oxime with high selectivity in H₂.^[16] The overall sequence of reactions to obtain nitrones from oximes is, however, complex, as the α,β-unsaturated nitro compound must be first prepared from a nitroalkane and an aldehyde (or ketone) by the Henry reaction followed by two additional reaction steps (Scheme 1A, route c). Recently, a new method for the preparation of cyclohexanone oxime directly from nitrobenzene has been reported.^[17] Otherwise, the synthesis of nitrones by oxidation of imines or secondary amines involves a multistep process, which often

[*] L. Cisneros, Dr. P. Serna, Dr. A. Corma
Instituto de Tecnología Química
Universidad Politécnica de Valencia-Consejo Superior de Investigaciones Científicas
Avda. de los Naranjos s/n, 46022 Valencia (Spain)
E-mail: psername@itq.upv.es
acorma@itq.upv.es
Homepage: <http://itq.upv-csic.es/>

[**] The research was supported by Project CONSOLIDER INGENIO (MULTICAT), PROMETEO, the SEVERO OCHOA Program for centers of excellence, the "Subprograma Ramon y Cajal" (contract RYC-2012-10662 to P.S.), and the CONACyT Program (fellowship to L.C.).

Supporting information for this article (including experimental details and additional characterization) is available on the WWW under <http://dx.doi.org/10.1002/anie.201402878>.

starts with the reduction of a nitro compound at the earliest reaction steps (Scheme 1 A, route a).

Alternatively, the production of nitrones from a nitro compound reduced in the presence of aldehydes is a more direct and atom-efficient route, whereby hydroxylamine generated in situ reacts with the carbonyl compound in a cascade-type reaction. This approach circumvents hydroxylamine storage issues and minimizes the number of experimental steps, but requires a catalyst that prevents the complete reduction of the NO₂ group, the hydrogenation of the aldehyde, and the degradation of the nitrone via secondary reaction paths (Scheme 1 B). The approach has been proved to work with stoichiometric reagents such as Zn dust,^[18] but then large amounts of waste are generated. The discovery of a solid catalyst that affords the nitrone in high yields, directly from nitro compounds, aldehydes, and H₂, would be of interest.

Herein we describe the design of a selective solid metal catalyst by controlling the characteristics of the support and the metal particle architecture to avoid other competing reactions. Specifically, this catalyst consists of platinum nanoparticles that exclude atoms of high coordination for interaction with the reactants, as well as supports that activate the nitroaromatic compound and its reduced derivatives. This control of the catalytic selectivity in complex fine-chemistry processes by manipulation of a solid catalyst is unusual.^[19]

Table 1 summarizes the catalysts that we tested using the coupling of nitrobenzene with 5-methylfurfural as a model reaction. We investigated Au/TiO₂, Pt/TiO₂, and Pt/C catalysts, which, properly prepared,^[20a–c] are highly selective for the hydrogenation of NO₂ groups, together with other common supported metal catalysts. The percentage value that accompanies each catalyst in this paper refers to a nominal weight percent metal content. Selectivities and conversions mentioned in the text are calculated based on gas chromatography data. Yields of isolated products are also reported in Table 2.

Despite their expected tolerance of the carbonyl function,^[20a] gold nanoparticles supported on TiO₂ showed low selectivity to nitrone formation (15%) and, instead, the imine **4** was obtained preferentially (Table 1), in agreement with previous reports.^[21] The reaction temperature required with the Au/TiO₂ catalyst is relatively high (373 K) due to the limited capacity of gold for activating H₂ in the presence of the nitroaromatic compound.^[22] We noticed that the use of high temperatures causes the selectivity to nitrone **3** to decrease (Table S1).

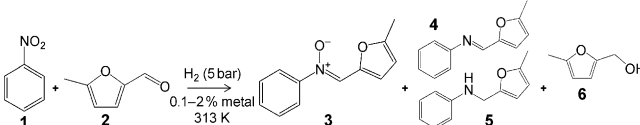
By switching from gold to platinum we were able to tackle the reaction at lower temperatures (298–308 K). Unfortunately, attempts to use typical (commercially available) supported metal catalysts to obtain the nitrone were fruitless. For example, the reaction with 5 wt % Pt/Al₂O₃ (Aldrich) at 308 K and 5 bar of H₂ gave nitrone **3** with low selectivity (6%; Table 1) and the secondary amine **5** as the predominant reaction product. This catalyst, moreover,

caused a notable loss of selectivity due to reduction of 5-methyl furfural to alcohol **6**.

Remarkably, the nitrone selectivity could be increased after controlling the structure of the metal active sites and the characteristics of the support. For example, at 308 K and 5 bar, platinum nanoparticles supported on TiO₂ (0.2 wt % Pt) activated at 573 K in H₂ provide 72% selectivity to nitrone **3** at almost complete conversion of the aldehyde, along with the imine **4** as the main by-product. When the same catalyst was activated in H₂ at a higher temperature (723 K), the nitrone selectivity dropped to 57% under identical experimental conditions and similar conversion (the imine was, again, the most significant by-product). No loss of selectivity due to hydrogenation of the carbonyl function of 5-methyl furfural was observed in these cases.

The decay in selectivity as the Pt/TiO₂ catalyst is activated in H₂ at the highest temperature (723 K) takes place with the concomitant appearance of TiO_x species on top of the Pt nanoparticles, as evidenced by HRTEM, EDS analysis, and IR spectroscopy (Figures S1 and S2). This decoration effect indicates the occurrence of strong metal–support interactions, typical of supports that are reducible metal oxides,^[23] which increases the contact area between Pt and TiO₂. The detrimental effect of the metal/support boundary on nitrone selectivity is consistent with the role attributed to TiO₂ in minimizing the formation of hydroxylamine during the hydrogenation of nitro compounds^[24] and, thus, in minimizing the hydroxylamine–aldehyde condensation path (Scheme 1).

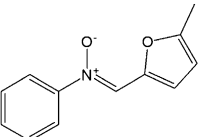
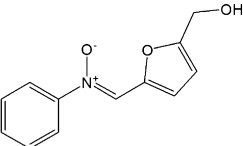
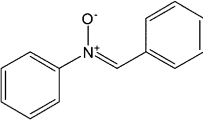
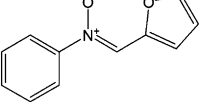
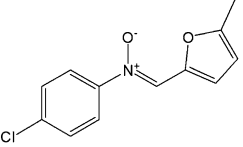
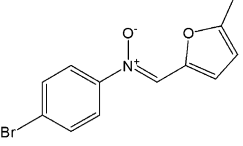
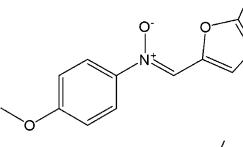
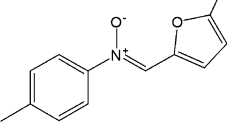
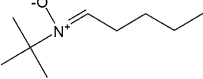
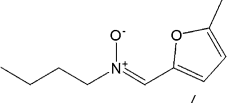
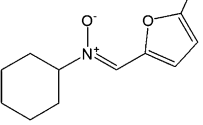
Table 1: Catalytic performance^[a] of various catalysts for the reductive coupling of nitrobenzene and 5-methyl furfural to nitrone **3**.



Catalyst ^[b]	Metal [%] ^[g]	t [h]	Conv. [%]	Selectivity [mol %] ^[h]			
				nitrone 3	imine 4	amine 5	alcohol 6
1% Au/TiO ₂ ^[c,d]	0.50	3.0	95	15	69	11	3
5% Pt/Al ₂ O ₃ -CM	2.5	2.0	97	6	4	57	15
0.2% Pt/TiO ₂ ^[e]	0.11	0.7	99	72	25	3	0
0.2% Pt/TiO ₂ ^[f]	0.20	0.5	98	57	42	1	0
0.2% Pt/Al ₂ O ₃	0.20	1.7	98	78	3	12	6
5% Pt/Al ₂ O ₃	1.01	1.3	97	51	5	30	13
0.2% Pt/C	0.18	1.1	100	97	3	0	0
0.2% Pt/graphite	0.12	0.9	80	74	4	14	6
2% Ru/C	1.95	4.3	95	84	14	0	0
0.2% Pd/C	0.10	0.7	93	82	8	8	0
5% Pd/Al ₂ O ₃ -CM	4.6	2.0	54	0	0	61	39
1% Pd/C-CM	0.48	3.0	93	6	0	93	1

[a] Reactions performed at 308 K and 5 bar of H₂, unless otherwise indicated. Feed composition (mol %): 90.5% ethanol, 6% nitrobenzene, 3% 5-methyl furfural, 0.5% o-xylene. [b] Catalysts activated in H₂ flow at 723 K, unless otherwise indicated. The notation CM refers commercially available samples. Metal content given as a nominal weight percent. [c] Activated in air at 673 K. [d] Tested at 373 K and 8 bar. [e] Activated in H₂ at 473 K. [f] Activated in H₂ flow at 723 K, leading TiO_x-decorated Pt nanoparticles. [g] (mol of metal)/(mol of 5-methyl furfural) × 100 [h] Determined by GC analysis. Balance corresponds to small amounts of unidentified products.

Table 2: Catalytic performance^[a] of 0.2 wt % Pt/C reduced in H₂ at 723 K for the reductive coupling of various nitro compounds and aldehydes.

Product	<i>t</i> [h]	Conv. [%] ^[b]	Sel. [%] ^[b]	Yield [%] ^[c]
	1.1	99	97	86
	1.5	99	89	76
	1.3	98	96	87
	0.5	99	94	85
	2.0	98	96	86
	0.4	97	92	88
	1.0	98	90	79
	0.6	99	95	85
	4.5	91	51	n.d. ^[d]
	13.0	90	50	43
	14	96	27	24

[a] Typical feed composition (mol): 90.5 % ethanol, 6 % nitro compound, 3 % aldehyde, 0.5 % *o*-xylene (internal standard). 50 mg of catalyst per 900 mg of feed. See the Supporting Information for the exception with the bromine-substituted nitron. [b] Conversion and selectivity calculated based on gas chromatography. [c] Yield of isolated product determined for scaled-up reactions (16 g of feed). [d] Not determined.

Consistent with our inference, the yield of nitron could be increased when a non-reducible metal oxide, Al₂O₃, served as the support for the platinum nanoparticles. In the absence of a strong metal–support interaction, the selectivity to nitron was 78 % at 98 % conversion using a 0.2 wt % Pt/Al₂O₃ catalyst. We detected other differences in the product distribution depending on the support, as the 0.2 wt % Pt/TiO₂ sample produces the imine **4** as the main by-product, whereas 0.2 wt % Pt/Al₂O₃ forms significant amounts of the secondary amine **5** (through further reduction of the N=C group). We stress, moreover, that despite the overall higher nitron selectivity of the 0.2 wt % Pt/Al₂O₃ catalyst, this sample is not completely selective for reduction of the nitro group of nitrobenzene over the carbonyl group of 5-methylfurfural. Indeed, alcohol **6** is produced in 5 % yield; it was not produced with the 0.2 wt % Pt/TiO₂ catalyst.

Additional experiments pointed to differences in product distribution as a function of the architecture of the platinum nanoparticles. To obtain Pt nanoparticles with different average crystallite size on Al₂O₃, the metal content on the surface of Al₂O₃ was varied from 0.2 wt % to 5 wt %, followed by reduction of the catalyst in H₂ at 723 K. Results are shown in Figure 1. The microscopy images show that the fraction of species larger than 2 nm is negligible in the 0.2 wt % Pt/Al₂O₃ catalyst, whereas particles within the range 2–4 nm are more abundant in the 5 wt % Pt/Al₂O₃ sample, together with some aggregates larger than 15 nm (Figure 1 A,B). IR spectra of the Pt/Al₂O₃ catalysts probed with CO show that the ratio of low-coordination Pt atoms (band centered at 2056 cm^{−1})^[25] to atoms on terrace positions (band centered at 2070 cm^{−1})^[26] is greater in the 0.2 wt % Pt/Al₂O₃ catalyst, as expected for metal nanoparticles that are, on average, smaller. Together with these bands, a less intense signal at about 1825 cm^{−1} is observed for both samples, which is ascribed to CO species bridging platinum sites of the nanoparticles.^[26]

When the results obtained with the 0.2 wt % and 5 wt % Pt/Al₂O₃ samples are compared for the reaction of nitrobenzene and 5-methyl furfural in H₂, 78 % and 51 % selectivity to nitron **3** is obtained, respectively, at high conversion of the aldehyde (Table 1). Thus, we infer that the presence of extended platinum surfaces has a negative impact on the nitron selectivity. Moreover, the 5 wt % Pt/Al₂O₃ catalyst produces larger amounts of the alcohol **6**, which agrees well with earlier reports pointing to a loss of chemoselectivity in the hydrogenation of nitro groups when the number of platinum terrace sites is increased.^[20a]

From all the above, we infer that to avoid products other than the nitron the catalyst should contain neither an activating support nor terrace Pt atoms. As will be shown, we achieved such a catalyst using a high-surface-area carbon as the support.

Deposition of 0.2 wt % Pt onto porous active carbon (Darco KB-B, 100 mesh), followed by reduction in H₂ at 723 K, results in the formation of small crystallites that range from 0.6 to 3.5 nm in diameter, as determined by STEM (Figure 1 C). Interestingly, whereas the particle size distribution of this catalyst and that of the 0.2 wt % Pt/Al₂O₃ sample are similar, the IR spectrum of the former (probed with CO) indicates that the carbon-supported sample consists of more

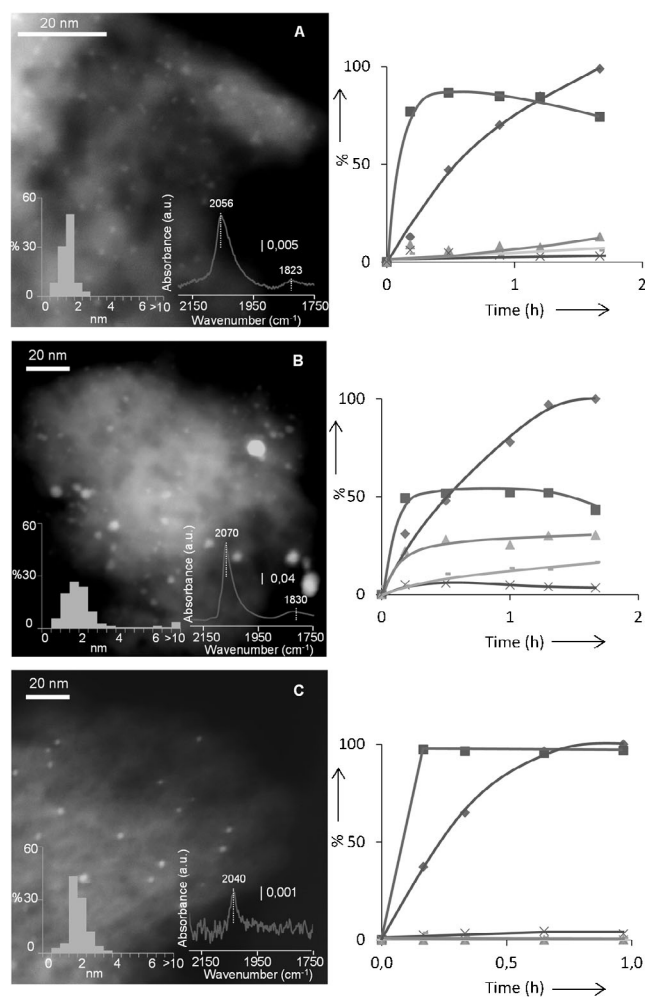


Figure 1. STEM images, particle size histograms, and IR spectra of the following catalysts: A) 0.2 wt % Pt/Al₂O₃; B) 5 wt % Pt/Al₂O₃; and C) 0.2 wt % Pt/C. IR spectra were recorded after probing the catalysts with CO at 298 K. Kinetic curves (right hand) correspond to conversion of 5-methyl furfural (diamonds), and selectivities to nitrone (squares), imine (crosses), secondary amine (triangles) and 5-methyl furfuryl alcohol (dash) during the reductive coupling of nitrobenzene and 5-methyl furfural at 308 K and 5 bar.

highly unsaturated Pt species (band at 2040 cm⁻¹) and completely lacks sites attributable to Pt in terrace (>2050 cm⁻¹) or bridging (<1850 cm⁻¹) positions. HRTEM images of this sample reveal that the platinum nanoparticles are embedded in the pores of the support (Figure S2), and we infer that the lack of terrace sites accessible to CO is due to the presence of carbon species covering the surface of the platinum nanoparticles. With only highly unsaturated platinum species exposed, almost quantitative yields to the nitrone is achieved (Table 1, 0.2 wt % Pt/C, 97 % selectivity at 100 % conversion). No hydrogenation of 5-methyl furfural is observed, corresponding to a catalyst that is highly chemo-selective.^[20a]

Consistent with the results above, when small platinum nanoparticles (1.4 ± 0.4 nm, Figure S3) were synthesized on a nonporous graphitic support (0.2 wt % Pt) by impregnation

with H₂PtCl₆ followed by reduction in H₂ at 723 K, the selectivity to nitrone **3** was only 74 % at 80 % conversion (Table 1). This catalyst behaves similar to the 0.2 wt % Pt/Al₂O₃ sample, both showing similar particle size distributions, and the secondary amine and 5-methyl furfuryl alcohol as the main by-products.

To investigate whether the preceding synthetic approach could be expanded to prepare selective catalysts with other metals, porous active carbon was used to support palladium and ruthenium. Accordingly, 0.2 wt % Pd/C and 0.2 wt % Ru/C samples led to selectivities to the nitrone of 80 and 84 %, respectively, at almost complete conversion of the aldehyde. These values are lower than those obtained with the 0.2 wt % Pt/C catalyst (Table 1), but remarkably better than those obtained with commercially available Pd catalysts (<6 %, Table 1).

Finally, the most selective Pt/C catalyst was tested for reactions of various nitro compounds and aldehydes in H₂ (Table 2). Good selectivities to the corresponding nitrones (>94 %) were obtained for reactions of aromatic aldehydes such as benzaldehyde, furfural, and 5-(hydroxymethyl) furfural with nitrobenzene. Nitrobenzenes incorporating electron-withdrawing group such as Cl and Br also yielded the halide-substituted nitrones in high yields (94 % and 90 %, respectively) in the presence of 5-methylfurfural, with no dehalogenation side reactions. Good results were obtained as well with substrates having electron-donating such as 4-nitroanisole and 4-nitrotoluene (88 and 93 % yield, respectively). Aliphatic nitro compounds showed lower nitrone selectivities (30–50 %), as a parallel reduction of the carbonyl function was then observed. We note that some of the products, such as *N*, α -diphenyl nitrone and its derivatives,^[5,7,10–13] are very useful building blocks in organic synthesis, and some nitrones reported here for the first time may contribute to expand the scope of applications.

While the catalyst provides only moderate selectivity with nitroalkanes, we would like to highlight the remarkable selectivity of the 0.2 wt % Pt/C catalyst for the formation of aromatic nitrones in the presence of alkenes and alkynes. For example, mixtures of nitrobenzene, 5-methyl furfural, and styrene (or phenylacetylene) yielded the nitrone in high yields with very little hydrogenation of the C=C (or C \equiv C) bond (<2 %; Table 3). In contrast, other catalysts, such as 0.2 wt % Pt/Al₂O₃ or 0.2 wt % Pd/C, caused a fast and complete reduction of styrene (or phenylacetylene) before the nitrone reaction could be completed. The compatibility of the 0.2 wt % Pt/C catalyst with alkenes and alkynes is relevant, because the latter and nitrones are susceptible to 1,3-dipole cycloadditions giving isoxazolidines or isoxazolines, and, from them, important β -amino alcohols could be synthesized.^[4]

In conclusion, we show that platinum nanoparticles can be tuned to synthesize nitrones selectively directly from nitro compounds, aldehydes, and H₂. This is accomplished by hindering the accessibility of the reactant to platinum on terrace positions of the nanoparticles and by avoiding supports that activate the nitro compound to minimize the hydroxylamine intermediate.

Table 3: Reductive coupling of nitrobenzene and 5-methylfurfural in the presence of styrene or phenylacetylene^[a] using various catalysts at 308 K and 5 bar of H₂.

Catalyst ^[b]	Cosubstrate	t [h]	C=C or C≡C conv. [%] ^[c]	Nitrone yield [%] ^[d]
0.2 wt% Pt/C	styrene	1.0	1	96
0.2 wt% Pt/C	phenylacetylene	1.1	2	95
0.2 wt% Pt/Al ₂ O ₃	phenylacetylene	1.3	100	22
0.2 wt% Pd/C	phenylacetylene	0.3	100	27

[a] 900 mg of a feed with the following molar composition: 87.5 % ethanol, 6 % nitrobenzene, 3 % 5-methylfurfural, 3 % styrene (or phenylacetylene), and 0.5 % *o*-xylene (internal standard). [b] Catalyst loading: 50 mg per experiment. [c] Conversion of styrene or phenylacetylene due to C=C or C≡C hydrogenation. [d] Determined by gas chromatography.

Received: February 28, 2014

Revised: May 15, 2014

Published online: July 9, 2014

Keywords: cascade reactions · hydrogenation · supported catalysts · nitrones

- [1] "Organic Free Radicals": E. G. Janczen, C. A. Evans, E. R. Davis in *ACS Symposium Series, Vol. 69* (Ed.: W. A. Prior), American Chemical Society, Washington, D.C., **1978**, p. 433.
- [2] G. Scott, K. V. Smith, *Eur. Polym. J.* **1978**, *14*, 39–43.
- [3] K. J. Lee, D. H. Kim, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 323–326.
- [4] K. V. Gothelf, K. A. Jorgensen, *Chem. Rev.* **1998**, *98*, 863–909.
- [5] J. Marco-Contelles, *Angew. Chem. Int. Ed.* **2004**, *43*, 2198–2200; *Angew. Chem.* **2004**, *116*, 2248–2250.
- [6] G. Masson, P. Cividino, S. Py, Y. Vallée, *Angew. Chem. Int. Ed.* **2003**, *42*, 2265–2268; *Angew. Chem.* **2003**, *115*, 2367–2370.
- [7] a) D. A. Evans, H.-J. Song, K. R. Fandrick, *Org. Lett.* **2006**, *8*, 3351–3354; b) D. Carmona, M. P. Lamata, F. Viguri, R. Rodriguez, L. A. Oro, F. J. Lahoz, A. I. Balana, T. Tejero, P. Merino, *J. Am. Chem. Soc.* **2005**, *127*, 13386–13398; c) A. Gawade, S. Bhunia, R.-S. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 7835–7838; *Angew. Chem.* **2012**, *124*, 7955–7958; d) I. S. Young, M. A. Kerr, *Angew. Chem. Int. Ed.* **2003**, *42*, 3023–3026; *Angew. Chem.* **2003**, *115*, 3131–3134; e) Y. Qian, X. Xu, X. Wang, P. J. Zavalij, W. Hu, M. P. Doyle, *Angew. Chem. Int. Ed.* **2012**, *51*, 5900–5903; *Angew. Chem.* **2012**, *124*, 6002–6005; f) F. Cardona, A. Goti, *Angew. Chem. Int. Ed.* **2005**, *44*, 7832–7835; *Angew. Chem.* **2005**, *117*, 8042–8045; g) F. Liu, D. Qian, L. Li, X. Zhao, J. Zhang, *Angew. Chem. Int. Ed.* **2010**, *49*, 6669–6672; *Angew. Chem.* **2010**, *122*, 6819–6822.
- [8] J. Hamer, A. Macaluso, *Chem. Rev.* **1964**, *64*, 473–494.
- [9] a) R. W. Murray, M. J. Singh, *Org. Chem.* **1990**, *55*, 2954–2957; b) M. Shun-Ichi, M. Hitoshi, S. Tatsuki, T. Tomoyasu, S. Watanabe, *J. Org. Chem.* **1990**, *55*, 1736–1744.
- [10] S. Cicchi, A. Goti, A. Brandi, *J. Org. Chem.* **1995**, *60*, 4743–4748.
- [11] D. Christensen, K. A. Jorgensen, *J. Org. Chem.* **1989**, *54*, 126–131.
- [12] A. Dondoni, S. Franco, F. Junquera, F. L. Merchan, P. Merino, T. Tejero, *Synth. Commun.* **1994**, *24*, 2537–2550.
- [13] E. Buehler, *J. Org. Chem.* **1967**, *32*, 261–265.
- [14] a) A. Melman in *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids* (Eds.: Z. Rappoport, J. F. Liebman), Wiley, Chichester, UK, **2008**; b) O. Kamm, *Org. Synth.* **2008**, *1*, 445–447.
- [15] H.-U. Blaser, H. Steiner, M. Studer, *ChemCatChem* **2009**, *1*, 210–221.
- [16] A. Corma, P. Serna, H. García, *J. Am. Chem. Soc.* **2007**, *129*, 6358–6359.
- [17] P. Rubio-Marqués, J. C. Hernández-Garrido, A. Leyva-Pérez, A. Corma, *Chem. Commun.* **2014**, *50*, 1645–1647.
- [18] V. Gautheron-Chapoulaud, S. U. Pandya, P. Cividino, G. Masson, S. Py, Y. Vallée, *Synlett* **2001**, 1281–1283.
- [19] M. M. Nigra, I. Arslan, A. Katz, *J. Catal.* **2012**, *295*, 115–121.
- [20] a) A. Corma, P. Serna, P. Concepción, J. J. Calvino, *J. Am. Chem. Soc.* **2008**, *130*, 8748–8753; b) A. Corma, P. Serna, *Science* **2006**, *313*, 332–334; c) P. Serna, M. Boronat, A. Corma, *Top. Catal.* **2011**, *54*, 439–446.
- [21] L. L. Santos, P. Serna, A. Corma, *Chem. Eur. J.* **2009**, *15*, 8196–8203.
- [22] P. Serna, P. Concepción, A. Corma, *J. Catal.* **2009**, *265*, 19–25.
- [23] a) S. J. Tauster, S. C. Fung, R. Garten, *J. Am. Chem. Soc.* **1978**, *100*, 170–175; b) G. L. Haller, D. E. Resasco, *Adv. Catal.* **1989**, *36*, 173–235.
- [24] a) A. Corma, P. Concepción, P. Serna, *Angew. Chem. Int. Ed.* **2007**, *46*, 7266–7269; *Angew. Chem.* **2007**, *119*, 7404–7407; b) M. Boronat, P. Concepción, A. Corma, S. Gonzalez, F. Illas, P. Serna, *J. Am. Chem. Soc.* **2007**, *129*, 16230–16237.
- [25] J. Sarkany, R. D. Gonzalez, *Appl. Catal.* **1983**, *5*, 85–97.
- [26] a) T. Jin, Y. Zhou, G. J. Mains, J. M. White, *J. Phys. Chem.* **1987**, *91*, 5931–5937; b) F. Boccuzzi, A. Chiorino, E. Guglielminotti, *Surf. Sci.* **1996**, *368*, 264–268.