

Highly selective conversion of hydroxylated biaryls to dibenzofuran derivatives over zeolite catalyst

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Zeolite HSZ-360 promotes the conversion of hydroxylated biaryls to dibenzofuran derivatives in satisfactory yields and excellent selectivities. Clays and amorphous silica–alumina are inert or less effective.

Introduction

The dibenzofuran system is a fundamental framework of various natural products¹ and show considerably interesting properties such as atropisomerism.² The main synthetic approach to dibenzofurans utilizes derivatives of biphenyl and, in particular, the Lewis or protic acid-promoted ring closure of biphenyl-2,2'-diols represents one of the most important routes to these compounds.³ This method, however, frequently suffers from harsh reaction conditions, low yields and the use of expensive catalysts.

Results and discussion

Employment of zeolites and clays in organic synthesis has received considerable attention in the last few years.⁴ This is due to the fact that reactions with these catalysts are environmentally benign, operationally simpler, economically more convenient and often show high yield and selectivity.

Since the use of solid acids for the preparation of fine chemicals is currently the subject of active investigation within our group,⁵ we studied the dehydration of hydroxylated biaryls to dibenzofurans over different heterogeneous catalysts. The results are reported herein.

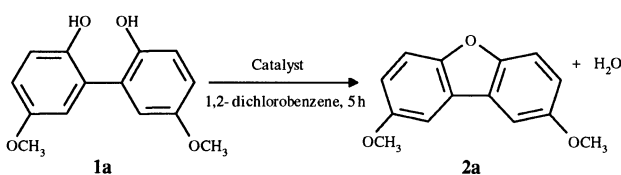
To achieve the optimum conditions for the process, 2,2'-dihydroxy-5,5'-dimethoxybiphenyl **1a** was treated under different conditions in the presence of the following heterogeneous catalysts: montmorillonite KSF (Fluka),⁶ silica gel grade 60 and acid alumina (Aldrich), amorphous silica–alumina (see Table 1) and zeolite HSZ-360 (H-form) [Tosoh Corp.]. All catalysts were activated at 120 °C under vacuum for 10 h before use. Reactions were carried out by heating, at the selected temperature for 5 h, a mixture of diol **1a** (2.46 g, 0.01 mol), the catalyst (1 g) and 1,2-dichlorobenzene (20 ml). In all experiments the product **2a** and unchanged starting biaryl **1a** were the sole detectable compounds (GLC) (see Table 1).

Upon using montmorillonite KSF only traces of compound **2a** were observed (Table 1, entry 1). Product **2a** was not obtained when silica and acid alumina were utilized (Table 1, entries 2 and 3). Use of zeolite HSZ-360 gave compound **2a** and the reaction temperature had a notable effect on the conversion of the reagent **1a**; in particular, the production of compound **2a** increased with the temperature (Table 1, entries 5–7).

HSZ-360 is a commercial acid faujasite-type zeolite with a high SiO₂/Al₂O₃ molar quotient of 13.9,⁷ pore size 8 Å,⁷ surface area 480–510 m²/g,⁸ acidity 0.2 mequiv. H⁺/g⁹ and is currently utilized in petrochemical processes and Friedel–Crafts reactions.

The effect of the hardness and the structure of the acid catalyst is interesting. Since use of an amorphous silica–alumina

Table 1 Dehydration of 2,2'-dihydroxy-5,5'-dimethoxybiphenyl **1a** to 2,8-dimethoxydibenzofuran **2a** over different solid acids



Entry	Catalyst	T/°C	Yield 2a (%)	Recovered 1a (%)
1	Montmorillonite KSF (Fluka)	100	6	91
2	SiO ₂ (Aldrich)	100		55
3	Al ₂ O ₃ (Aldrich)	100		18
4	Amorphous silica–alumina 15 ^a	100	3	92
5	Zeolite HSZ 360 (Tosoh)	100	30	62
6	Zeolite HSZ 360 (Tosoh)	140	39	53
7	Zeolite HSZ 360 (Tosoh)	180	48	42

^a Amorphous silica–alumina 15 (SiO₂/Al₂O₃ molar quotient = 15) was prepared by adding to a stirred solution of 10% aluminium nitrate a colloidal silica solution (30% wt SiO₂), followed by co-precipitation of SiO₂ and Al(OH)₃ with NH₄OH (2 M) up to pH ~ 8.2. The solid was then filtered off, washed with water, dried overnight at 120 °C and finally calcined in air at 700 °C for 16 h.

with surface area 190 m²/g and acidity 0.50 mequiv. H⁺/g afforded compound **2a** in ~3% yield (Table 1, entry 4), the Brønsted acid effect is not the sole factor responsible for activation of the reagents and we can conclude, in agreement with previously reported studies, that catalytically active sites in the zeolite are stronger than in the corresponding amorphous materials.¹⁰

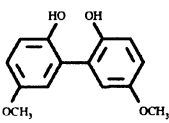
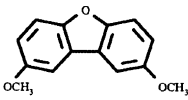
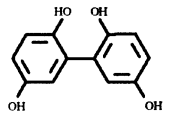
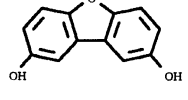
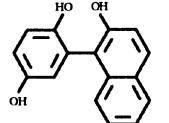
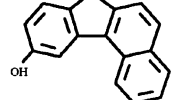
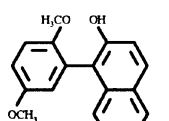
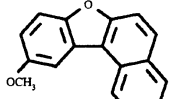
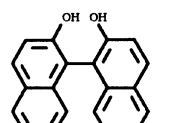
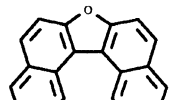
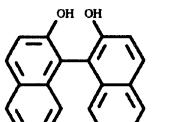
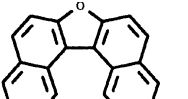
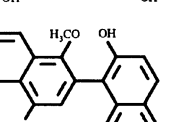
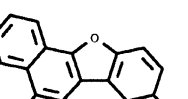
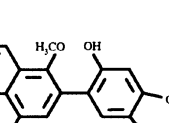
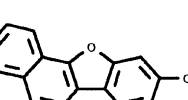
The synthetic versatility of the reaction was further established by employing substituted hydroxylated biaryls **1a–h** under the best conditions reported in Table 1 (entry 7). Results are reported in Table 2.

The starting reagents **1a–h** were prepared by metal-templated oxidative coupling of phenols¹¹ or regioselective addition of metal phenolates to quinones or quinone ketals.¹²

Results from Table 2 suggest that dibenzofuran derivatives **2a–h** are obtained in satisfactory to good yields and that the reaction is conveniently performed with electron-rich biaryls. Since conversion of biaryls **1** into dibenzofurans **2** over acid catalysis is an electrophilic reaction, substrates bearing electron-withdrawing substituents are expected to be inert. Thus chloro derivatives were recovered unchanged.

Both hydroxylated and methoxylated biaryls gave dibenzofurans with loss of water or methanol, and only methoxy groups involved in the ring closure undergo demethylation when polymethoxylated substrates are utilized. On the other

Table 2 Synthesis of dibenzofuran derivatives **2** from hydroxylated biaryls **1** promoted by zeolite HSZ-360

Entry	Reagent 1	Dibenzofuran derivative 2	Yield (%)
a			48
b			33
c			77
d			42
e			100
f			50
g			75
h			60

hand the demethylation process is more difficult to control in the reaction promoted by Lewis or protic acids.³

Though the exact mode of the reaction is not clear at this point, we may formulate a mechanism based on the generally accepted theory of electrophilic ring closure.^{3a} The initial step is believed to involve acid–base interaction of the substrate **1** with the catalyst, affording the active aryl cation by protonation at the 3- or 5-position of the more electron-rich aromatic ring of the reagent **1**. The subsequent intramolecular nucleophilic attack of the 2'-hydroxy group on the C-2 of the protonated aromatic ring leads to the cyclic product **2** with loss of water.

Concerning the role of the catalyst, at present it is not possible to demonstrate exactly the inclusion of all biaryls **1** into the cages and channel system of zeolite HSZ-360 and thus it is impossible to state if the reaction occurs in the pores or on the external surface of the catalyst. In fact, compound **1a**¹¹ is small enough to enter and move through the channels of the catalyst (pore dimension 8 Å); on the other hand bulkier compounds such as **1e** and **1f** are probably more difficult to accommodate in the pores.

Nevertheless, some significant data emerge from the results in Tables 1 and 2. The reaction is performed only with highly electron-enriched aromatic rings. Clays such as montmorillonites are ineffective. Finally, as previously demonstrated for different acid-promoted reactions, zeolites show higher catalytic activity than do the amorphous silica–alumina catalysts.¹⁰

In summary we have shown a simple and easy synthesis of dibenzofuran derivatives **2** starting from electron-rich hydroxylated biaryls **1** and the commercially available zeolite HSZ-360. It is noteworthy that the process tolerates the presence of methoxy and methylenedioxy groups.

Experimental

Mps were obtained on an Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded on Nicolet PC5 FT-IR spectrophotometer. ¹H NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz. Chemical shifts are expressed in ppm relative to tetramethylsilane as internal standard, and *J*-values are expressed in Hz. Mass spectra were recorded on a Finnigan SSQ 710 instrument in CI mode.

TLC analyses and chromatography were performed on Merck PF₂₅₄ silica gel, using hexane–ethyl acetate mixtures.

Gas chromatographic analyses were performed on a Dani 8221-a instrument [SPB-1 Supelco column; 30 m; 80 °C (2), 15 °C/min, 280 °C] connected to a Hewlett-Packard HP 3396A integrator.

Microanalyses were carried out by Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica dell'Università di Parma.

Compounds **1a–e,g,h** were prepared as reported in the literature.^{11,12}

Synthesis of 2,2',6,6'-tetrahydroxy-1,1'-binaphthyl **1f**

A solution of 2,6-dihydroxynaphthalene (0.01 mol, 1.60 g) in dry nitromethane (20 ml) was added to a stirred solution of AlCl₃ (0.01 mol, 1.33 g) in dry nitromethane (20 ml) under nitrogen. After 30 min, a solution of anhydrous FeCl₃ (0.01 mol, 1.62 g) in dry nitromethane (20 ml) was added and the mixture was stirred for 5 h at room temperature. The reaction was quenched with 2 M HCl (60 ml) and the resulting mixture was extracted with methylene dichloride (3 × 50 ml). The organic phase was dried (Na₂SO₄), the methylene dichloride was distilled off, and the residue was chromatographed on a silica gel column with 50/50 hexane–ethyl acetate as eluent to give a solid, (decomp. before melting) (Found: C, 75.7; H, 4.3. C₂₀H₁₄O₄ requires C, 75.5; H, 4.4%); ν_{\max} (KBr)/cm⁻¹ 3437; δ_{H} (300 MHz; CD₃OD) 7.79 (2 H, dd, *J* 9.1 and 2.5, 7- and 7'-H), 6.90 (2 H, d, *J* 9.1, 8- and 8'-H), 7.12 (2 H, d, *J* 2.5, 5- and 5'-H), 7.20 (2 H, d, *J* 8.9, 3- and 3'-H) and 7.66 (2 H, d, *J* 8.9, 4- and 4'-H); *m/z* 319 (M⁺ + 1, 100%), 187 (23) and 159 (42).

Synthesis of dibenzofuran derivatives **2**

General procedure. To a solution of the selected hydroxylated biaryl **1** (10 mmol) in dry 1,2-dichlorobenzene (20 ml), 1 g of zeolite HSZ-360 was added and the reaction mixture was stirred for 5 h at reflux. After cooling, the reaction mixture was filtered and the catalyst was washed with methylene dichloride (100 ml); the solvent was distilled off under reduced pressure and the crude residue was chromatographed on a silica gel column with 20–60% hexane–ethyl acetate as eluent to give the following products.

2,8-Dimethoxydibenzofuran **2a**: solid, mp 89–90 °C (lit.,¹³ 89–90 °C).

2,8-Dihydroxydibenzofuran **2b**: solid, mp 242.5–243.5 °C (lit.,¹³ 239–240 °C).

10-Hydroxybenzo[*b*]naphtho[1,2-*d*]furan **2c**: solid, mp 159–159.5 °C (lit.,¹³ 160 °C).

10-Methoxybenzo[b]naphtho[1,2-d]furan **2d**: solid, mp 70–71 °C (Found: C, 82.5; H, 4.7. C₁₇H₁₂O₂ requires C, 82.2; H, 4.9%); δ_{H} (300 MHz; CDCl₃) 3.88 (3 H, s, OCH₃), 6.99 (1 H, dd, *J* 8.9 and 2.6, 9-H), 7.44 (1 H, sym. m, 3- or 2-H), 7.47 (1 H, d, *J* 8.9, 8-H), 7.60 (1 H, d, *J* 9.0, 6- or 5-H), 7.61 (1 H, sym. m, 2- or 3-H), 7.68 (1 H, d, *J* 2.6, 11-H), 7.76 (1 H, d, *J* 9.0, 5- or 6-H), 7.89 (1 H, d, *J* 8.1, 4- or 1-H) and 8.40 (1 H, d, *J* 8.1, 1- or 4-H); *m/z* 249 (M⁺ + 1, 100%) and 205 (8).

Dinaphtho[2,1-*b*:1',2'-*d*]furan **2e**: solid, mp 154–155.5 °C (lit.¹⁴ 154 °C).

3,11-Dihydroxydinaphtho[2,1-*b*:1',2'-*d*]furan **2f**: pale brown solid, mp 270–272 °C (Found: C, 80.3; H, 4.2. C₂₀H₁₂O₃ requires C, 80.0; H, 4.0%); ν_{max} (KBr)/cm⁻¹ 3307; δ_{H} (300 MHz; CDCl₃, CD₃OD) 7.3–7.4 (4 H, m, 2-, 4-, 10- and 12-H), 7.7–7.8 (4 H, m, 5-, 6-, 8- and 9-H) and 8.99 (2 H, d, *J* 8.8, 1- and 13-H); *m/z* 301 (M⁺ + 1, 12%), 199 (28) and 171 (100).

12-Methoxydinaphtho[1,2-*b*:1',2'-*d*]furan **2g**: pale brown solid, mp 189–192 °C (Found: C, 84.3; H, 4.9. C₂₁H₁₄O₂ requires C, 84.5; H, 4.7%); δ_{H} (300 MHz; CDCl₃) 4.20 (3 H, s, OCH₃), 7.5–7.8 (4 H, m, 10-, 9-, 3- and 2-H), 7.69 (1 H, s, 13-H), 7.84 (1 H, d, *J* 8.9, 6- or 5-H), 7.89 (1 H, d, *J* 8.9, 5- or 6-H), 8.03 (1 H, d, *J* 8.1, 11- or 8-H), 8.40 (1 H, d, *J* 8.4, 4- or 1-H), 8.44 (1 H, d, *J* 8.7, 1- or 4-H) and 8.63 (1 H, d, *J* 8.3, 8- or 11-H); *m/z* 298 (M⁺, 100%).

5-Methoxy-8,9-methylenedioxybenzo[b]naphtho[2,1-*d*]furan **2h**: pale brown solid, mp 143–146 °C (Found: C, 74.3; H, 4.2. C₁₈H₁₂O₄ requires C, 74.0; H, 4.1%); δ_{H} (300 MHz; CDCl₃) 4.08 (3 H, s, OCH₃), 6.04 (2 H, s, CH₂), 7.12 (1 H, s, 6- or 10- or 7-H), 7.15 (1 H, s, 10- or 7- or 6-H), 7.27 (1 H, s, 7- or 6- or 10-H), 7.50 (1 H, ddd, *J* 8.3, 7.0 and 1.2, 3- or 2-H), 7.62 (1 H, ddd, *J* 8.1, 7.0 and 1.2, 2- or 3-H), 8.28 (1 H, d, *J* 8.1, 1- or 4-H) and 8.33 (1 H, d, *J* 8.3, 4- or 1-H); *m/z* 292 (M⁺, 100%).

Acknowledgements

We acknowledge the support of the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST), Italy, and the Consiglio Nazionale delle Ricerche (CNR), Italy. We are

grateful to the Centro Interdipartimentale Misure (CIM) for the use of NMR and mass instruments.

We thank Mr Pier Antonio Bonaldi for technical assistance.

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Paper 6/07282H

Received 25th October 1996

Accepted 16th December 1996