Pergamon

Tetrahedron 54 (1998) 14757–14766

TETRAHEDRON

Zeolite-Catalyzed Acylation of Heterocyclic Compounds – VI. One-step Synthesis of 3-(benzofuran-2-carbonyl)pentane-2,4-dione from 2-acetylbenzofuran over HY-zeolite.

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1:UMR 6503 – Catalyse en Chimie Organique

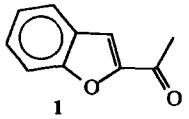
2:UMR 6514 – Synthèse et Réactivité des Substances Naturelles

Received 17 April 1998; accepted 29 September 1998

Abstract: *The reaction between 2-acetylbenzofuran and acetic anhydride at 60°C in the presence of HY-zeolite (Si/Al = 16) led to a single final product:3-(benzofuran-2-carbonyl)pentane-2,4-dione resulting from two consecutive acylation steps on the side chain. It was obtained in a 90% purity at around 50% conversion of 2-acetylbenzofuran. Other minor products and intermediates were also identified. A mechanism is proposed to account for the formation of the various products.*

INTRODUCTION

Solid acid catalysts, like zeolites, can offer definite advantages over soluble ones. They are easy to recover and produce no salts.[1-3] HY-zeolites with Si/Al atomic ratios of 15 to 20[4-10], as well as beta zeolites[10], are active catalysts for the acylation under mild conditions of heterocyclic compounds. In the acylation of benzofuran with acetic anhydride over HY-zeolite, significant amounts of secondary products (mainly di- and triacylated) were found at high conversion.[9] These compounds were shown to be formed by acylation of the primary product, 2-acetylbenzofuran **1**, which at high conversion led to a single triacylated product. This product was actually identified as being 3-(benzofuran-2-carbonyl)pentane-2,4-dione **2**, a β-triketone which could be of interest as chelating agent. Therefore it appeared interesting to investigate the acylation of 2-acetylbenzofuran **1** under the same conditions in order to obtain a better insight in the reaction scheme of the acylation of benzofuran and to try to obtain selectively triacylated benzofuran.



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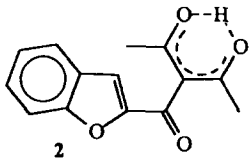

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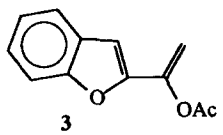

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RESULTS

Reaction of 2-acetylbenzofuran with acetic anhydride

Preliminary experiments in the absence of any catalyst gave no reaction. Figure 1 shows the conversion of **1** *versus* reaction time in the presence of HY-zeolite. The reaction gives one main product and three minor products and intermediates, all of which can be separated by gas liquid chromatography. At the end of the experiment (8 hours), a conversion of about 30% was obtained. This corresponds to approximately 4.1 mol

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PII: S0040-4020(98)00904-1

per mol of acid site (as determined by ammonia titration). The shape of the curve in Figure 1 indicates that the catalyst deactivated quite rapidly. This result is similar to the one reported by Smith *et al.*[11] for the acylation of 2,3-dimethyl-2-butene over HY zeolite. However, as shown previously, this can be attributed to the irreversible adsorption of heavy products (coke) rather than to the effect of acetic anhydride or acetic acid.[6,9] Actually, the deactivation process was not the same for the acylation of 2-methylbenzofuran as for the acylation under the same conditions of benzofuran. If acetic acid were responsable for deactivation, the phenomenon would be expected to be the same in the both cases. However, as for the acylation of benzofuran or 2-methylbenzofuran,[9] the catalyst could be recovered after use, regenerated by calcination and reused without any loss in activity. By changing the amount of catalyst and the reaction time, a wide range of conversion was obtained (up to 50%), as shown in Figure 2.

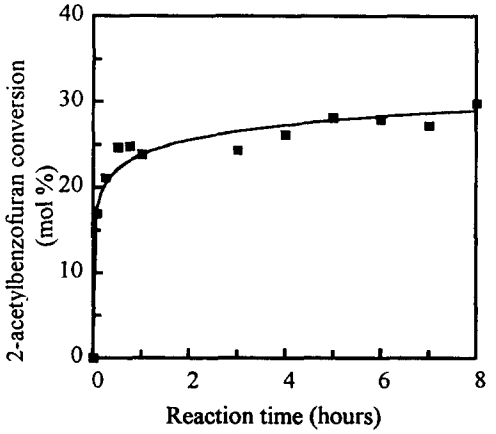


Figure 1: Reaction of 2-acetylbenzofuran **1** (3.125 mmol) with acetic anhydride (105 mmol) over HY-zeolite (0.5g) at 60°C.

The reaction leads to a single final product: 3-(benzofuran-2-carbonyl)pentane-2,4-dione **2**, with three intermediates (Figure 2). Actually, there is just one primary product, 1-acetoxy-1-(benzofuran-2-yl)ethene, **3** (Figure 2b). Two other minor products appear at higher conversion of **1**. These two compounds, **4** and **5**, were identified as enolacetates of β-diketone **6**. They were also obtained by direct acetylation of **6** in Ac_2O catalyzed by traces of *p*-toluenesulfonic acid. These two compounds were in equilibrium and are presumably *Z-E* stereoisomers. They transform ultimately into β-triketone **2** which was obtained in 90% selectivity at around 50% conversion.

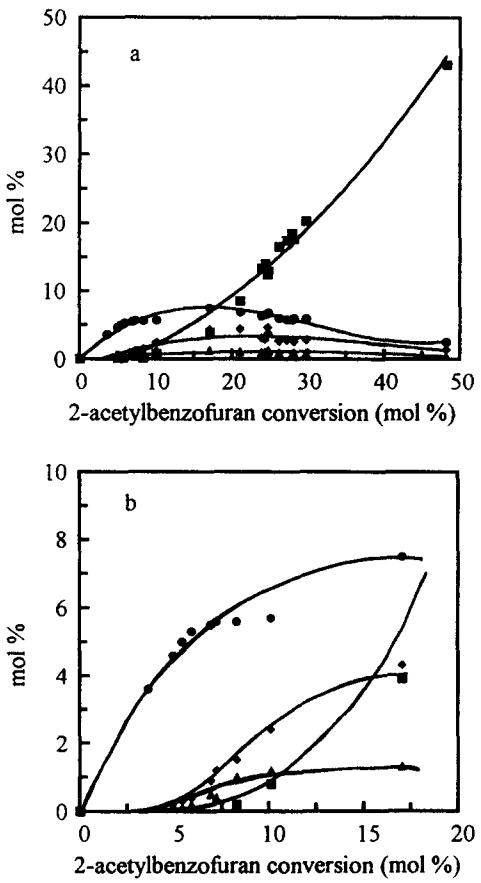


Figure 2: Reaction of **1** with acetic anhydride over HY-zeolite (Si/Al = 16, 0.1-1g) at 60°C. Effect of conversion on product distribution. ■: β-triketone **2**; •: acetate **3**; ♦: acetate **4**; ▲: acetate **5** (a: overall reaction; b: products formed at low conversion).

Transformation of 1-acetoxy-1-(benzofuran-2-yl)ethene 3

To better understand the path of the reaction, compound **3** was prepared,[12] and was let to react under the same experimental conditions as compound **1**. The conversion of **3** was immediate (Figure 3) and gave

initially acetates **4** and **5** which then disappeared, contributing to the formation of the final product **2**. However acetate **3** mainly decomposes into 2-acetylbenzofuran, which shows that the reaction between the latter and acetic anhydride is easily reversible under our reaction conditions. Under these experimental conditions, the formation of β-triketone **2** is irreversible. Traces of β-diketone **6** were also detected.

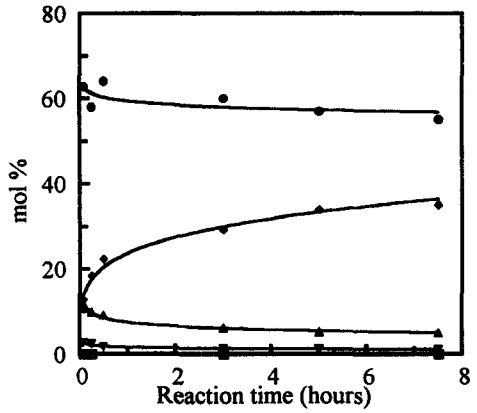
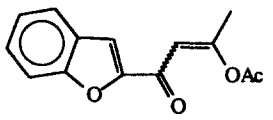
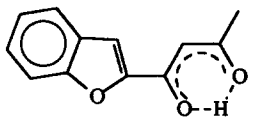


Figure 3: Reaction of acetate **3** (1 mmol) with acetic anhydride (53 mmol) over HY-zeolite (0.5 g). •: 2-acetylbenzofuran **1**; ♦: β-triketone **2**; ▲: enolacetate **4**; ▼: enolacetate **5**; ■: β-diketone **6**.



4, 5



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Transformation of 1-(benzofuran-2-yl)butane-1,3-dione 6

The compound **6** was tested as a possible intermediate for the formation of β-triketone **2**. It was even more reactive than acetate **3** under the same experimental conditions, in less than 10 minutes, it was totally converted giving mainly the final product **2** (80 mol%) and compound **4** (20 mol%). This indicates that compound **6** must be an intermediate in this reaction.

Identification of the products

The reaction products were identified by conventional spectroscopic methods. Their main characteristics are presented in Table 1.

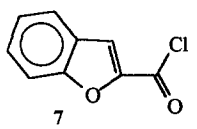
In mass spectrometry, these compounds were characterized by a typical (M^+-42) fragmentation. This fragmentation was the typical one observed for acetates **3**, **4** and **5**. Two other fragmentations were also detected with β-diketone **6** and β-triketone **2**: (M^+-15) and (M^+-17) which correspond respectively to the loss of -CH_3 and -OH fragments from the enol form.[13]

The ^{1}H NMR spectra present a signal between 6.7 and 7.7 ppm corresponding to the five aromatic protons of the benzenic and heterocyclic rings. It can also be noticed that β-diketone **6** and β-triketone **2** exist mainly in their enol forms with intramolecular hydrogen bonds, as shown by the signals appearing respectively at 15.5 and 17.0 ppm. Both methyl groups of the keto-enolic form of **2** appear as a singlet in ^{1}H and ^{13}C NMR at δ_H = 2.13 and δ_C = 24.34 ppm. Therefore, in Scheme 1, products **2** and **6** are represented in their keto-enol forms with intramolecular hydrogen bonds. The main product and the intermediates were prepared by independent synthetic methods[12,14-17] in order to ascertain their structures and to examine their reactivities under the same conditions as for 2-acetylbenzofuran. Compound **2** was prepared by reacting the corresponding acyl chloride **7** on pentane-2,4-dione enolate.[16] Compound **6** was obtained through reaction of trimethylsilylated enol **8** with ethanal[15] followed by Jones oxidation of **9**.[17]

Table 1: Spectroscopic characteristics of the products obtained by reaction of 2-acetylbenzofuran with acetic anhydride over HY-zeolite (CBV720).

	mass spectroscopy		^{1}H NMR			^{13}C NMR	
compound	m/z	fragments	δ_H (ppm)	intensity	group	δ_C (ppm)	group
	M: 244		2.13	6H	$-CH_3$	24.34	$-CH_3$
2	M - 17	-OH	17.02	1H	=C-OH	192.64	C=O
	M - 18	$-H_2O$					
	M - 42						
3	M: 202		2.29	3H	$-OCOCH_3$	20.81	$-CH_3$
	M -42	"$-COCH_2$"	5.17	1H	$=CH_2$	150.46	=C-O
			5.77	1H	$=CH_2$	168.47	C=O
4	M: 244		2.33	3H	$=C-CH_3$		
	M -42	"$-COCH_2$"	2.42	3H	$-OCOCH_3$		
			6.77	1H	=CH-		
5	M: 244		2.26	3H	$=C-CH_3$		
	M -42	"$-COCH_2$"	2.50	3H	$-OCOCH_3$		
			6.88	1H	=CH-		
	M: 202		2.23	3H	$-COCH_3$	193.25	C=O
6	M - 15	$-CH_3$	6.3	1H	=CH-		
	M - 17	-OH	15.48	1H	=C-OH		
	M - 42						

2: 3-(benzofuran-2-carbonyl)pentane-2,4-dione; 3: 1-acetoxy-1-(benzofuran-2-yl)ethene; 4 and 5: enolacetates of 6; 6: 1-(benzofuran-2-yl)butane-1,3-dione.



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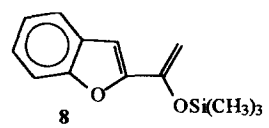

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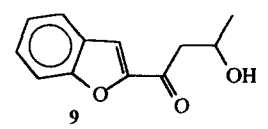

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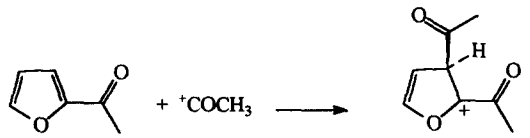
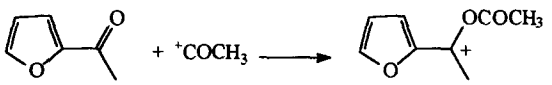
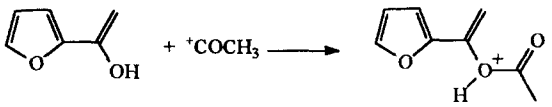
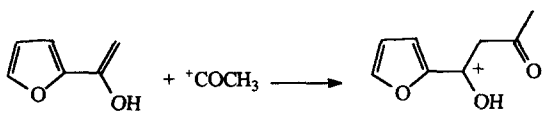
Theoretical model

In order to clarify some aspects of the reaction mechanism, *ab initio* calculations were performed. Because of the complexity of the system, some simplifications were made on the theoretical model: the zeolite framework was neglected and energies of reaction were calculated instead of activation parameters. The aim of this calculation was to answer the following questions: i) is the second acylation more efficient on the 3 position of the benzofuran moiety or on the acyl group? ii) does the second acylation involve a *C*-acylation or an *O*-acylation?

Ab initio calculations were carried out using the Gaussian 94 package.[18] The equilibrium structures were optimized at the restricted Hartree-Fock (RHF) level with the standard 3-21G basis set. To obtain more reliable energies of reaction, density functional calculations were performed on the RHF geometry. For this purpose, the B3LYP method, also available in Gaussian 94, was used[19] with 6-13G plus polarization basis set. Small effects like thermal and zero point energy corrections were neglected. The results for model reactions are collected in Table 2. The model reactions have very different energies of reaction. Interactions with the zeolite and the solvent are not expected to modify significantly the relative values of these energies of reaction.

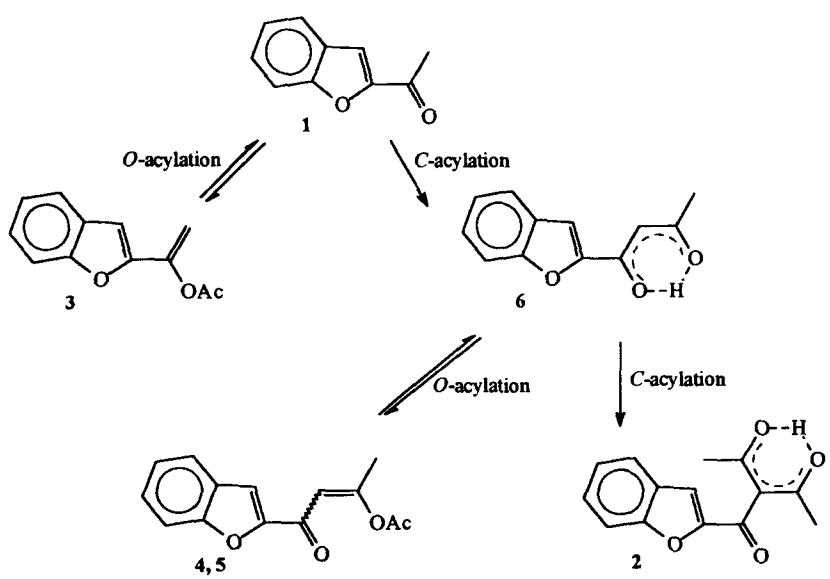
Table 2: Energies of reaction for *O*- and *C*-acylation of 2-acetylfuran (*ab initio* calculations).[20]

Reaction enthalpies	ΔH (kJ.mol^{-1})
	-42
	-205
	-88
	-255

DISCUSSION

Reaction scheme

The following reaction scheme (Scheme 1) can be postulated.



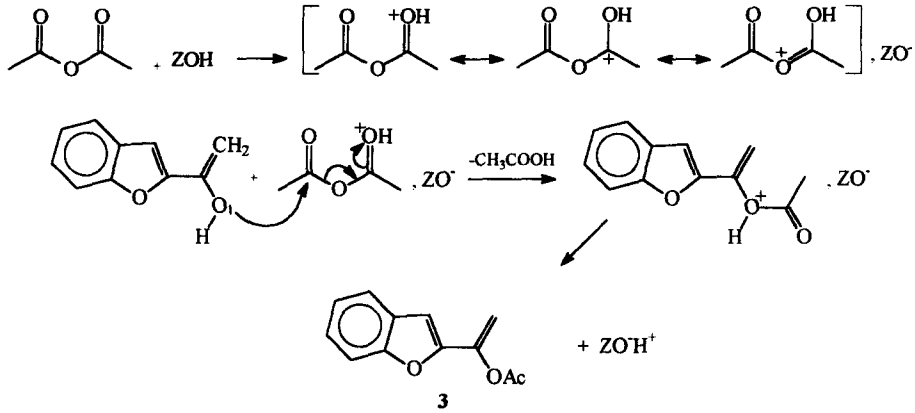
Scheme 1. Reaction of 2-acetylbenzofuran with acetic anhydride over HY-zeolite at 60°C.

As expected because of the deactivating properties of the acyl group, the electrophilic substitution did not occur on the aromatic ring but on the acyl group (either by *O*- or *C*-acylation). *Ab initio* calculations show that the substitution on the acyl group is more exothermic than the attack in position 3 of 2-acetylfuran by about 160 kJ.mol^{-1} (Table 2). It is also well known that *O*-acylation is usually faster than *C*-acylation.[21] Therefore acetate **3** was formed more rapidly than β-diketone **6** and its formation which could occur through esterification of the enol form of **1**, was found to be reversible under our experimental conditions. This is why its concentration never surpassed 7 mol %. This behavior can be expected for every product formed by *O*-acylation, *e.g.* acetates **4** and **5** from β-diketone **6**. Therefore these compounds disappear at high conversion, the equilibrium being shifted because of the irreversible formation of the final product **2** (scheme 1).[22]

β-Diketone **6** was found to be highly reactive under the operating conditions and this explains why it was not found at the end of the reaction.

Formation of the monoacylated products 3 and 6.

The role of the zeolite is to activate the acylating reagent on its protonic sites. This reaction is followed by an acylium ion transfer through a Rideal-type mechanism as shown in Scheme 2 for the formation of **3**.



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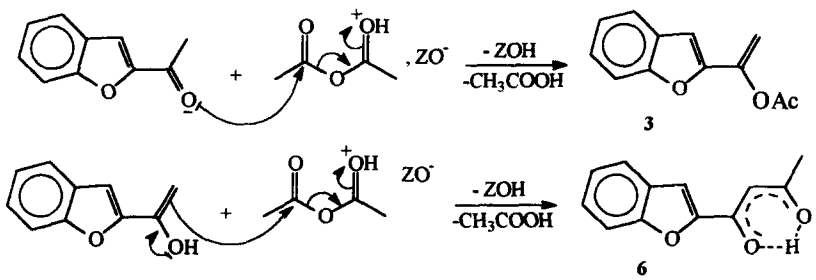
Scheme 2. Rideal type mechanism for the *O*-acylation of 2-acetylbenzofuran. Formation of **3**.

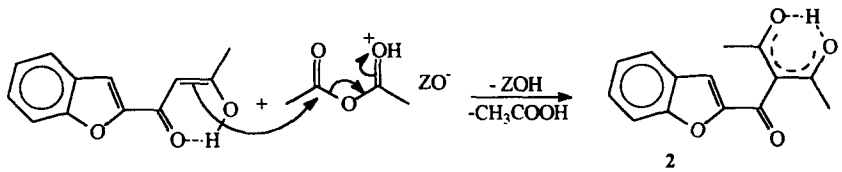
O-acylation could occur either on the ketone or on its enol form as shown in Scheme 2. *Ab initio* calculations made in the case of 2-acetylfuran show that the ketone form has a greater stability than the enol form by about 84 kJ.mol^{-1}. Moreover, in the case of 2-acetylfuran, the *O*-acylation on the ketone is more exothermic than the *O*-acylation on the enol (Table 2). However, the calculations show that the *C*-acylation of the enol is even more exothermic than the *O*-acylation of the ketone. This may compensate for the fact that the enol is probably in low concentration and explain why β-diketone **6** could be formed at a significant rate and be an intermediate for the formation of the diacylated products **4** and **5**. Hence the two monoacylated compounds would be formed as indicated in Scheme 3.



Scheme 3. Reaction of 2-acetylbenzofuran. Formation of the monoacylated products.

Formation of the diacylated products 2, 4 and 5.

The esterification of the enol form of compound **6** leads to the acetates **4** and **5** which are probably *Z-E* isomers. *C*-acylation of **6** leads to the β-triketone **2** (Scheme 4).



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Scheme 4. Reaction of 2-acetylbenzofuran with acetic anhydride. Formation of the β-triketone **2**.

CONCLUSION

The β-triketone **2** can be obtained in one step (50% conversion, 90% purity) by reaction of 2-acetylbenzofuran **1** with acetic anhydride in the presence of HY-zeolite.

The reaction involves mainly one intermediate (β-diketone **6**) which by *O*-acylation leads to by-products and by *C*-acylation leads to the expected final product. The formation of all the products resulting from *O*-acylation is reversible under our experimental conditions, which is not the case for β-triketone **2** resulting from *C*-acylation. This makes it possible to obtain a good selectivity in β-triketone **2** when conversion increases.

A mechanism involving protonated acetic anhydride which attacks the side chain of the substrate or intermediate accounts for the formation of the various products.

EXPERIMENTAL PART

Catalyst

The HY-zeolite used in this work was a commercial sample (CBV720) supplied by Conteka. The composition of the zeolite was determined by chemical analysis. The framework Si/Al atomic ratio was deduced from the unit cell parameter (determined by X-Ray diffraction, ASTM method D3942-80) using the equation given by Breck and Flanigen.[23] The unit cell formula of the zeolite deduced from its composition and Si/Al atomic ratio was $Na_{0.3}H_{11}Al_{11.3}Si_{180.7}O_{384}$ with 2.4 extraframework aluminum atoms per unit cell. The BET surface area (nitrogen adsorption) was 700 $m^2.g^{-1}$ and its pore volume was 0.43 $cm^3.g^{-1}$. The number of acid sites determined by ammonia titration was of 0.46 10^{-3} $mol.g^{-1}$, which means about twice less than the number deduced from the unit cell formula.

Chemicals

2-Acetylbenzofuran (99%), acetic anhydride (99%) and benzofuran-2-carboxylic acid (99%) were purchased from Aldrich. They were used without further purification. The other substrates (reaction intermediates used as reactants) and the products to be identified were prepared according to the procedures indicated below.

Procedure

The zeolite was calcined at 500°C in a pretreatment reactor for 8 hours under dry air flow. The catalyst (0.5 g usually) was then transferred while hot into a 100 cm^3 batch reactor without exposure to the ambient atmosphere (by overturning the system under nitrogen flow). A solution of 2-acetylbenzofuran (501 mg, 3.12 mmol) in Ac_2O (10 cm^3, 105 mmol) was added to the freshly calcined zeolite, stirred and heated at 60°C. Samples were taken periodically and analyzed by gas liquid chromatography.

Gas chromatographic analysis

The samples were analyzed with a Varian 3400 chromatograph equipped with a BP1 capillary column (length, 30 m; diameter, 0.25 mm; film thickness, 0.25 μm). The oven temperature was programmed from 70

to 230°C (5°C.min^{-1}). The products were identified by adding aliquots of commercial or synthesized compounds or by GC/MS analysis.

Other experimental methods

To confirm the identification of the main products, the reaction mixture obtained in various experiments (at different conversion rates) was treated as follows. To eliminate the unreacted acetic anhydride and the acetic acid, the reaction mixture (about 10 cm^3) was treated with an aqueous $NaHCO_3$ solution (0.7 mol/l, 50 cm^3). The aqueous layer was extracted with CH_2Cl_2 (20 cm^3, twice), the combined organic fractions were dried over anhydrous Na_2SO_4 and CH_2Cl_2 was eliminated under vacuum. The products were then recovered by flash-chromatography (Silicagel 100-200 mesh, cyclohexane-ethyl acetate, 90:10) and by preparative thin layer chromatography (Kieselgel $60F_{254}$, 1 mm, Merck, cyclohexane-ethyl acetate, 90:10). The following recordings were made: *a*) ^{1}H and ^{13}C NMR spectra at 300 and 75 MHz respectively on a Bruker Advance BP X 300 spectrometer with $CDCl_3$ as solvent, *b*) mass spectra on a Finigan Matt INCOS 500 spectrometer with gas liquid chromatography coupling. The melting points were measured with a Büchi 510 apparatus using capillary tubes with a temperature program of 2°C.min^{-1}. They were not corrected. Microanalysis was performed at the CNRS Microanalysis Service (Vernaison, France) or with a NA2100 analyzer (C.E. Instrument).

Synthesis of the various intermediates and products.

1-acetoxy-1-(benzofuran-2-yl)ethene. [3]

The product was prepared according to Brewer and Elix.[12] mp: 48.5-49°C; mp[12]: oily product. **^{1}H NMR**: δ = 2.33 (s, 3H, -$COCH_3$); 5.17 (d, 1H, *J*=2.5Hz, =CHH); 5.77 (d, 1H, *J*=2.5Hz, =CHH); 6.68 (s, 1H, 3-H); 7.26 (m, 2H, 5-H and 6-H); 7.45 (d, 1H, *J*=6.7Hz, 7-H); 7.52 (d, 1H, *J*=7.8Hz, 4-H). **^{13}C NMR**: δ = 20.81 (-CH_3); 103.36 (3-C); 103.94 (=CH_2); 111.30 (7-C); 121.44 (4-C); 123.22 (5-C); 125.31 (6-C); 128.34 (9-C); 144.49 (2-C); 150.46 (=C-O); 155.25 (8-C); 168.47 (C=O). **MS**: m/z (%) = 202 (M^+, 26); 161 (11); 160 ([M-(CH_2CO)]$^+$, 100); 145 (11); 131 (32); 118 (10); 89 (8); 77 (10); 63 (10); 43 (61).

1-(Benzofuran-2-yl)-1-trimethylsilyloxyethene. [8]

According to the procedure described by Cazeau *et al.*,[14] a solution containing **1** (2.4 g, 15 mmol), anhydrous acetonitrile (3 cm^3), triethylamine (2.6 cm^3, 18.6 mmol) and trichloromethylsilane (2.35 cm^3, 18.6 mmol) was stirred for 15 min under N_2. Then, NaI (2.8 g, 18.6 mmol) in anhydrous acetonitrile (18 cm^3) was added dropwise. Stirring was maintained for 16 hours at room temperature. The crude product was diluted in cyclohexane (two layers), and filtered over silica gel. The solvent was eliminated under vacuum to produce an oily substance (2.73 g, 80%) which was used without further purification. **^{1}H NMR**: δ = 0.3 (9H, s, -$Si(CH_3)_3$); 4.57 (1H, d, *J*=1.6Hz, =CHH); 5.19 (1H, d, *J*=1.6Hz, =CHH); 6.76 (1H, d, *J*=0.6Hz, 3-H); 7.19 (1H, td, J_1=J_2=7.3Hz, J_3=1Hz, 5-H); 7.27 (1H, ddd, J_1=8Hz, J_2=7.3Hz, J_3=1Hz, 6-H); 7.44 (1H, dd, J_1=8Hz, J_2=1Hz, 7-H); 7.54 (1H, ddd, J_1=7.3Hz, J_2=1Hz, J_3=0.6Hz, 4-H).

1-(Benzofuran-2-yl)-3-hydroxybutan-1-one. [9].

According to the procedure described by Le Roux *et al.*,[15] a solution of $BiCl_3$ (189 mg, 0.59 mmol), NaI (266 mg, 1.77 mmol), acetaldehyde (0.73 cm^3, 12.9 mmol) and anhydrous CH_2Cl_2 (35 cm^3) was stirred under N_2 for 1 hour, until the solution became black. A solution of the previous enoxysilane **8** (2.73 g, 11.76 mmol) in anhydrous CH_2Cl_2 (40 cm^3) was then added. The solution was stirred overnight at room temperature, filtered over Celite, acidified with MeOH/HCl 1N (9:1, 40 cm^3), extracted with CH_2Cl_2, and finally dried over $MgSO_4$. The solvent was removed under vacuum to give an oily product (2.19 g). Flash-chromatography (eluent: ethyl acetate) yielded the alcohol (1.80 g, 75%). **^{1}H NMR**: δ = 1.32 (3H, d, *J*=6.2Hz, -CH_3); 3.09 (2H, d, *J*=6.2Hz, -CH_2-); 3.65 (1H, m, J_1=J_2=6.2Hz, -CHOH-); 4.45 (1H, s, -OH); 7.27 (1H, td, J_1=J_2=7.8Hz, J_3=0.9Hz, 5-H); 7.43 (1H, td, J_1=J_2=7.8Hz, J_3=1.1Hz, 6-H); 7.45 (1H, s, 3-H); 7.53 (1H, dd, J_1=7.8Hz, J_2=0.9Hz, 7-H); 7.66 (1H, dd, J_1=7.8Hz, J_2=1.1Hz, 4-H). **^{13}C NMR**: δ = 22.85 (-CH_3); 47.19 (-CH_2-); 64.12 (-CHOH-); 112.33 (3-C); 113.63 (7-C); 123.38 (4-C); 123.93 (5-C); 126.87 (6-C); 128.45 (9-C); 152.31 (2-C); 155.60 (8-C); 190.90 (C=O). **MS**: m/z (%) = 204 (M^+, 24); 186 (17); 161 (24); 160 (87); 147 (28); 145 (100); 131 (27); 118 (39); 89 (80); 77 (13); 63 (39); 43 (46).

1-(benzofuran-2-yl)butane-1,3-dione. [6]
The alcohol **9** (1.80 g, 8.8 mmol) dissolved in 20 cm^3 of acetone was oxidized with Jones reagent (CrO_3-H_2SO_4).[17] After usual workup, the crude product was purified by flash-chromatography (eluent: CH_2Cl_2) to yield the β-diketone **6** (0.98 g, 55%). mp 66-67°C. **^{1}H NMR**: δ = 2.23 (3H, s, -CH_3); 6.30 (1H, s, =C-H); 7.30 (1H, ddd, J_1=7.8Hz, J_2=7.8Hz, J_3=1Hz, 5-H); 7.43 (1H, td, J_1=J_2=7.8Hz, J_3=1.3Hz, 6-H); 7.48 (1H, d, J=1Hz, 3-H); 7.55 (1H, ddd, J_1=7.8Hz, J_2=1Hz, J_3=1Hz, 7-H); 7.69 (1H, complex d, J_1=7.8Hz, 4-H); 15.48 (1H, s, broad, =C-OH). **^{13}C NMR**: δ = 25.64 (-CH_3); 97.33 (=CH-); 111.11 (3-C); 111.94 (7-C); 122.69 (4-C); 123.74 (5-C); 125.87 (6-C); 127.38 (9-C); 150.83 (2-C); 155.30 (8-C); 174.12 (=C-OH); 193.25 (C=O). **MS**: m/z (%) = 202 (M^+, 100); 187 ([M-CH_3]$^+$, 60); 185 ([M-OH]$^+$, 31); 160 ([M-(CH_2CO)]$^+$, 30); 145 (76); 131 (20); 118 (21); 89 (49); 77 (23); 69 (77); 63 (34); 43 (71). **Analysis** cal. C 71.28 H 4.98 found C 71.10 H 4.98.

3-(benzofuran-2-carbonyl)pentane-2,4-dione. [2]
According to the procedure described by Womack and Mc Whirter,[16] a solution of benzofuran-2-carboxylic acid (0.80 g, 5 mmol) in freshly distilled $SOCl_2$ (6 cm^3) was poured into a round bottom flask equipped with a condenser and stirred for 16h at 70°C. HCl vapors were trapped at the exit of the cooler. Excess of reagent was eliminated under vacuum to yield benzofuran-2-carbonyl chloride **7** (0.90 g, 100%). A solution of pentane-2,4-dione (0.50 cm^3, 4.87 mmol) in anhydrous THF (5 cm^3) was added to sodium ethoxide (353 mg, 5.19 mmol) in anhydrous THF (10 cm^3). The solution was stirred for 16h at room temperature under N_2. Meanwhile, a white precipitate appeared and **7** (0.90 g, 5 mmol) in anhydrous THF (5 cm^3) was added dropwise. The solution became yellow and clear. After 1h, a saturated aqueous solution of NH_4Cl (40 cm^3) was added. After the usual procedure, the crude product was purified by flash chromatography (eluent:CH_2Cl_2) to yield 3-(benzofuran-2-carbonyl)pentane-2,4-dione **2** (0.80 g, 67%). mp: 61-61.5°C. **^{1}H NMR**: δ = 2.13 (6H, s, -CH_3); 7.35 (1H, td, J_1=J_2=8Hz, J_3=0.9Hz, 5-H); 7.52 (1H, td, J_1=J_2=8Hz, J_3=1.2Hz, 6-H); 7.53 (1H, d, J=1Hz, 3-H); 7.59 (1H, dd, J_1=8Hz, J_2=0.9Hz, 7-H); 7.72 (1H, ddd, J_1=8Hz, J_2=1.2Hz, J_3=1Hz, 4-H); 17.06 (1H, s, =C-OH). **^{13}C NMR**: δ = 24.34 (2x-CH_3); 112.49 (-C(=O)C=C(OH)-); 115.11 (3-C); 115.79 (7-C); 123.55 (4-C); 124.28 (5-C); 127.04 (6-C); 128.94 (9-C); 153.41 (2-C); 156.12 (8-C); 184.24 (2x=C-OH); 192.64 (C=O). **MS**: m/z (%) = 244 (M^+, 29); 229 ([M-CH_3]$^+$, 3); 227 ([M-OH]$^+$, 5); 226 ([M-H_2O]$^+$, 5); 202 ([M-(CH_2CO)]$^+$, 81); 187 (82); 185 (85); 160 (11); 145 (60); 131 (11); 118 (21); 89 (60); 77 (11); 69 (44); 63 (27); 43 (100). **Analysis** cal. C 68.85 H 4.95 found C 69.01 H 5.09.

Enolacetate of β-diketone 6. [4]
To 147 mg (0.7 mmol) of compound **6** dissolved in Ac_2O (1.5 cm^3) was added about 10 mg of *p*-TsOH. After ultrasonic stirring, the solution became strongly colored. After 70h at 35°C, the reaction mixture was poured in CH_2Cl_2 (40 cm^3) and this solution was washed with diluted sodium carbonate solution (10 cm^3). The organic phase was dried over $MgSO_4$ and evaporated to dryness under vacuum. The crystallized colored product was flash chromatographied (eluent: petroleum –AcOEt, 9:1) to afford acetate **4** (52 mg, 30%). mp: 113-114°C white needles (petroleum ether). **^{1}H NMR**: δ = 2.32 (3H, s); 2.41 (3H, s); 6.76 (1H, s); 7.09 (1H, s); 7.26 (1H, t, J=7.5Hz), 7.38 (1H, t, J=7.5Hz); 7.48 (1H, d, J=7.5Hz); 7.58 (1H, d, J=7.5Hz). **^{13}C NMR**: δ = 20.98 (-OCOCH_3); 31.88 (-CH_3); 110.02 and 111.53 and 111.73 (3-C and 5-C and –C(=O)C=C(OAc)-); 122.08 and 123.73 and 126.98 (4-C and 5-C and 6-C); 127.88 (9-C); 145.93; 149.55; 155.68 (8-C); 167.68(-C(=O)OR); 194.95 (R(C=O)-R'). **MS**: m/z (%) = 244 (M^+, 10); 202 ([M-(CH_2CO)]$^+$, 48); 187 (58); 185 (57); 145 (28);118 (13); 89 (28); 69 (39); 43 (100). **Analysis** cal. C 68.85 H 4.95 found C 69.14 H 5.00.

Spectroscopic characteristics of the synthesized compounds are identical to those of the compounds obtained in the experiments carried out with the zeolites (Table 1).

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