

Letter

Zeolite catalyzed acylation of heterocyclic compounds. Part III. Comparison between benzofuran and 2-methylbenzofuran

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Received 16 November 1994; accepted 19 May 1995

Abstract

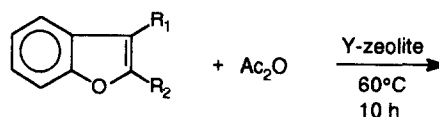
Benzofuran and 2-methylbenzofuran were acylated by acetic anhydride in the presence of Y-zeolite as catalyst (60°C, atmospheric pressure) with a 43% and 95% yield respectively.

Keywords: Acetic anhydride; Acylation; Benzofuran; 2-Methylbenzofuran; Zeolite

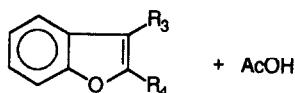
It was shown recently that Y zeolites could be used as catalysts for the acylation of benzofuran by acetic anhydride under mild conditions (batch reactor, 60°C) [1,2]. As pointed out recently [3,4], this method presents numerous advantages in environmental protection: the reaction produces a minimum of waste products (no salt) and the catalyst itself is easy to recover by filtration and to regenerate.

The results indicated that the reaction procedure strongly influenced the activity of the catalyst. It was shown that (a) the acylating agent has to be introduced before the substrate into the reactor containing the catalyst and the solvent [1] and (b) that increasing the concentration of the acylating agent could inhibit partly the catalyst deactivation due to the autocondensation of the substrate [2]. Hence it was concluded that acetic anhydride could be convenient both as solvent and as acylating agent.

In this paper, we compare the acylation of benzofuran and of 2-methylbenzofuran in the liquid phase (batch reactor). In both cases the major product is monoacylated and results from a substitution on the heterocycle: benzofuran (**1**) gives 2-acetylbenzofuran (**2**) and 2-methylbenzofuran (**3**) gives 3-acetyl-2-methylbenzofuran (**4**):



- 1** $R_1 = R_2 = H$
3 $R_1 = H; R_2 = CH_3$



- 2** $R_3 = H; R_4 = COCH_3$ 43%
4 $R_3 = COCH_3; R_4 = CH_3$ 95%

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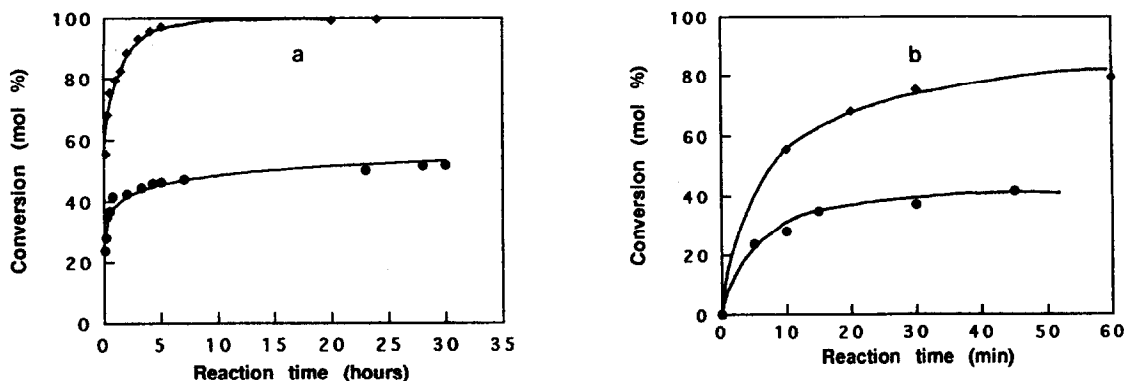


Fig. 1. Acylation of benzofuran (1, 14.5 mmol), and of 2-methylbenzofuran (3, 14.5 mmol) by Ac_2O (0.185 mol) over Y zeolite (0.5 g). Reaction conditions: batch reactor, 60°C, atmospheric pressure. Conversion of 1: ●; and of 3: ◆.

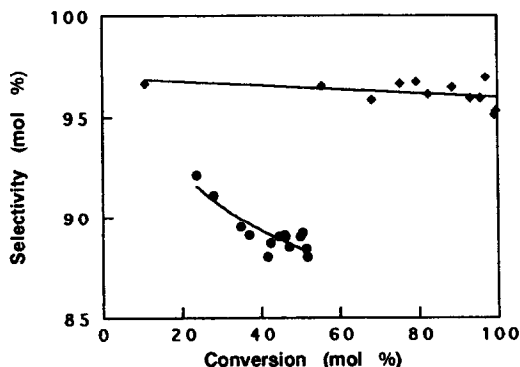


Fig. 2. Acylation of 1 (14.5 mmol) and of 3 (14.5 mmol) by Ac_2O (0.185 mol) over Y zeolite at 60°C in a batch reactor. Selectivity in 2-acetylbenzofuran (2): ●; and in 3-acetyl-2-methylbenzofuran (4): ◆.

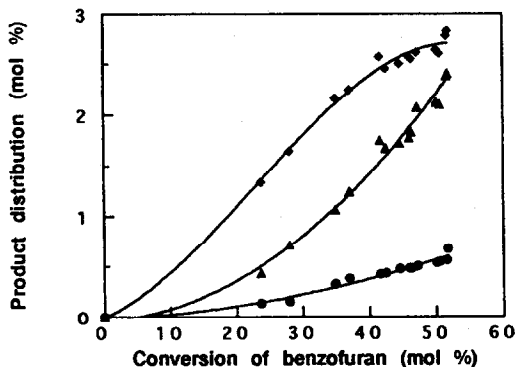


Fig. 3. Acylation of 1 (14.5 mmol) by Ac_2O (0.185 mol) at 60°C in a batch reactor. Distribution of the minor products. Monoacylated products (other than 2): ●; diacylated products: ◆; triacylated products: ▲.

The reaction probably occurs through a Friedel-Crafts mechanism involving the protonation of acetic anhydride on the acid sites of the zeolite followed by a Rideal type reaction with the substrate [1].

1. Experimental section

The reactions were carried out in a 100 cm³ stirred flask reactor under nitrogen. The zeolite ($\text{Na}_{0.3}\text{H}_{11}\text{Al}_{11.3}\text{Si}_{180.7}\text{O}_{384}$, 0.5 g) from Conteka (CBV720) was calcined in a flow reactor for 8 h under dry air and transferred into the batch reactor without exposure to ambient atmosphere by turning it upside down under nitrogen flow. The acylating agent (Ac_2O) used as solvent (0.185 mol) was added to the freshly calcined zeolite. The substrate (14.5 mmol) was added to the stirred mixture heated at 60°C. Samples were taken periodically and analyzed by GLC using a DB1 capillary-column (length: 30 m; diameter: 0.25 mm; film thickness: 0.25 μm). The products isolated by flash chromatography were identified by ¹H NMR and by gas chromatography coupled to mass spectrometry.

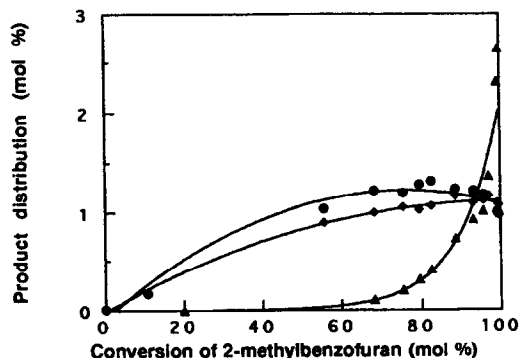


Fig. 4. Acylation of 3 (14.5 mmol) by Ac_2O (0.185 mol) at 60°C in a batch reactor. Distribution of the minor products. Monoacylated products (other than 4): ●; diacylated products: ◆; triacylated products: ▲.

As can be seen in Fig. 1, 2-methylbenzofuran (**3**) was much more reactive than benzofuran (**1**) under the same conditions. If initial rates are considered (Fig. 1b), it can be seen that 2-methylbenzofuran (**3**) was about twice as reactive as benzofuran (**1**). As shown in Fig. 1a, 100% conversion of **3** was obtained in about 10 h while the conversion of **1** ceased at about 50%.

The reaction was also very selective (Fig. 2) and actually more selective in the case of 2-methylbenzofuran (**3**) than in the case of benzofuran (**1**). This is not surprising since in the case of **3**, only one substitution position is available on the heterocycle. In fact it can be seen (Fig. 2) that up to 95% conversion the selectivity in **4** was over 95%. In the case of **1** the selectivity in **2** was lower (92% for a conversion of about 20%) and decreased more significantly when the conversion increased.

This was due mainly to the formation of 2,3-diacetylbenzofuran and triacylated products (Fig. 3). Very small quantities of the other monoacylated products were formed (0.5 to 1%). They seemed to be secondary products in the case of **1** (Fig. 3) and primary in the case of **3** (Fig. 4). Some diacylated (apparently primary) and triacylated (secondary) products were also formed in the case of **3** (Fig. 4).

Although, the 2-position, which is the most reactive in **1**, is blocked by the methyl group in **3**, the latter is still more reactive due to the donor effect of the methyl group. It should be noted however that since **1** gives only trace amounts ($\ll 1\%$) of 3-acetylbenzofuran, the 3-position in **3** is at least two orders of magnitude more reactive than in **1**.

As shown previously [2], the catalyst deactivated rapidly in the case of benzofuran (**1**) because of the building up of irreversibly adsorbed material (27 wt%) which was mainly made of acylated dimers or trimers of benzofuran (**1**) [2]. Such a phenomenon could be different in the case of **3** and could explain the difference in reactivity between the two substrates.

References

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