

Synthesis of aromatic ketones by acylation of aryl ethers with carboxylic anhydrides in the presence of zeolite H- β (H-BEA) in the absence of solvent ¹

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Abstract

The acylation of anisole, phenetole or diphenyl ether with carboxylic anhydrides at 100°C in the presence of catalytic quantities of zeolite H- β gives the corresponding *para*-acylated products in high yield; the zeolite can be recovered, regenerated and reused to give almost the same yield as that given by fresh zeolite. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Friedel-Crafts acylation is one of the most important methods for synthesis of aromatic ketones [1]. In general, Lewis acids or other catalysts are required in order to allow the reaction to proceed at a convenient rate. Ring acylation of aromatic ethers, for example, has been carried out in the presence of a variety of catalysts including aluminium chloride [2], polyphosphoric acid (PPA) [3], titanium tetrachloride [4], boron trifluoride [5] and others [6–13].

Unfortunately, use of such conventional catalysts involves a number of problems. For exam-

ple, ‘catalysts’ such as aluminium chloride are usually needed in more than stoichiometric amounts because of complexation to starting materials and/or products. Work-up often involves hydrolysis, which may lead to loss of the catalyst and cause problems with corrosion and disposal of potentially toxic wastes. Finally, reactions are not always clean and may lead to mixtures of products. The use of recoverable and regenerable solid catalysts such as zeolites can overcome many problems of these types. Therefore, the use of such catalysts in the manufacture of fine chemicals and chemical intermediates is gaining in importance [14,15]. For example, we have shown that zeolites or other solids can have advantages in chlorinations [16], brominations [17], allylations [18] and nitrations [19,20] of aromatic substrates.

Nevertheless, relatively little attention has

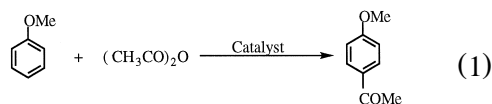
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¹ Dedicated to Professor Herman van Bekkum on the occasion of his 65th birthday.

been paid to the use of zeolites as catalysts in the acylation of aromatic compounds [21–27]. Acylation of anisole by acyl chlorides or carboxylic acids using 1 g of a zeolite per mmol of substrate in 50 ml of solvent gives modest yields of acylated product [24], while acylation of anisole with carboxylic acids over HZSM-5 at reflux for 48 h was reported to give two products (*p*-RCOC₆H₄OMe and RCO₂Ph) [28]. Clearly, there is still considerable scope for the development of superior methods which could be applicable on a commercial scale. The recent disclosure of the commercial application of a procedure involving zeolite-catalysed acylation of aromatic ethers [29] prompts us to report our own results in this area². We have been able to achieve the high yield acylation of anisole, phenetole and diphenyl ether with acid anhydrides under modest conditions over zeolite H-β in the absence of solvent.

2. Results and discussion

We first examined the effect of various acetylating agents on the acylation of anisole over zeolite H-β. It was clear from the results that acetic anhydride was the most effective reagent, giving a 55% yield of *p*-methoxyacetophenone (Eq. (1)) at 80°C under a particular set of conditions. A lower degree of acetylation occurred with acetyl chloride under the same conditions, while hardly any reaction occurred with ethyl acetate or acetic acid. Thus, acetic anhydride was selected for further studies.



The acylation of anisole with acetic anhydride was next carried out over various solid

catalysts, mostly zeolites. The results obtained are given in Table 1.

As the results in Table 1 show, the following order of activity was observed: H-β > HY > H-ZSM-5, H-Mordenite > K10 (an acidic clay) > Synclyst S23 (an amorphous acidic solid). Clearly, both zeolite H-β and zeolite HY were effective catalysts for the reaction, with other zeolites and solids being of lower value. Use of different cation-exchanged beta zeolites or of HY zeolites having different SiO₂/Al₂O₃ ratios did not result in any substantial improvement in activity. Zeolite H-β with a SiO₂/Al₂O₃ ratio of 25 was therefore selected for more detailed study. However, it should be recognized that the pores of zeolite HY allow readier diffusion than those of H-β. Therefore, for more hindered substrates and/or products HY may be more effective than H-β.

For the economic use of the reaction it would be beneficial to utilise the minimum quantity of the zeolite, and a series of reactions was therefore conducted in which the amount of zeolite H-β was varied. The results are shown in Table 2.

From the results it is clear that even a very small amount of H-β was capable of catalysing the reaction although the yield of product was greater, under the same conditions, the greater the amount of catalyst used. On the assumption that the rate of reaction should depend linearly on the amount of catalyst, it would appear that

Table 1
Yield of *p*-methoxyacetophenone according to Eq. (1) over various catalysts^a

Catalyst	Yield (%) ^b
Synclyst S23	4
K10	21
H-Mordenite	(34) ^c
H-ZSM-5 zeolite	35
H-β zeolite	76
HY zeolite	51

^aAnisole: Ac₂O: catalyst = 1 mmol: 1 mmol: 0.050 g, 100°C, 1 h, no solvent.

^bYield of isolated purified product unless otherwise stated.

^cBy quantitative GC.

² A verbal account of some of these results was presented at the 4th International Symposium on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, September 8–12, 1996.

Table 2
Effect of quantity of catalyst^a

Amount of zeolite (g)	Yield of <i>p</i> -methoxyacetophenone (%) ^b
0.005	29
0.025	46
0.050	55
0.150	61
0.250	75

^aAnisole (5 mmol), Ac₂O (5 mmol), with the catalyst for 1 h at 100°C.

^bBy quantitative GC.

the extent of reaction does not increase as rapidly as might be expected with increased amounts of catalyst. This is thought to be a result of (reversible) deactivation by the acetic acid formed as a byproduct. For further study the amount of catalyst was chosen to be 0.030 g per mmol of substrate.

The effect of temperature was next investigated. The results are shown in Table 3.

From the results in Table 3 it is clear that the reaction proceeds to some extent even at low temperature, but the yield under otherwise identical conditions is much greater at higher temperatures up to about 120°C. A temperature of 120°C was therefore chosen to investigate the effect of reaction time. The results are shown in Table 4.

From the results in Table 4 it is clear that at 120°C a high yield (98%) of *p*-methoxyacetophenone could be obtained in 2 h with as little as 0.030 g of catalyst per mmol of substrate. Alternatively, we have shown that excess acetic

Table 4
Effect of reaction time in Eq. (1)^a

Reaction time (h)	Yield of <i>p</i> -methoxyacetophenone (%) ^b
0.1	54
0.25	66
0.5	77
0.75	83
1.0	88
1.5	94
2	98
2.5	98
3	97

^aAnisole (5 mmol) was heated at 120°C with the zeolite (0.15 g) and acetic anhydride (5 mmol) for the given time.

^bThe yield was determined by GC.

anhydride (ca. 30%) can be used to encourage the reaction to completion within 1.5 h at 120°C or that the reaction can be conducted at a somewhat lower temperature (100°C) for a rather longer time.

It was of interest to see if the reaction was general. Therefore, the reactions of anisole, phenetole and diphenyl ether with various carboxylic acid anhydrides were conducted under standard conditions (Eq. (2)). The products were isolated by distillation and fully characterised. The results are shown in Table 5.

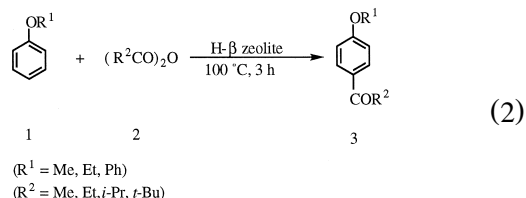


Table 3
Effect of temperature in Eq. (1)^a

Temp. (°C)	Yield of <i>p</i> -methoxyacetophenone (%) ^b
20	5
50	19
60	28
90	54
100	67
120	93
Reflux	87

^aAnisole (5 mmol), Ac₂O (5 mmol), H-β (0.15 g), 1.5 h at the indicated temperature.

^bBy GC.

As can be seen from Table 5, the reactions were successful with acetic, propionic and isobutyric anhydrides and for phenetole and diphenyl ether as well as anisole, but the acylation of anisole and phenetole with trimethylacetic anhydride gave only poor yields of the corresponding aromatic ketones, and the acylation of diphenyl ether with trimethylacetic anhydride did not take place at all under the reaction conditions, presumably due to steric hindrance. No attempt was made to optimise individual reactions, but it is likely that higher yields in the

Table 5
Reactions of aromatic ethers with anhydrides according to Eq. (2)^a

R1	R2	Yield of product (%) ^b
Me	Me	76
Me	Et	73
Me	<i>i</i> -Pr	73
Me	<i>t</i> -Bu	10
Et	Me	77
Et	Et	74
Et	<i>i</i> -Pr	75
Et	<i>t</i> -Bu	14
Ph	Me	52
Ph	Et	43
Ph	<i>i</i> -Pr	27
Ph	<i>t</i> -Bu	0

^aThe aryl ether (30–50 mmol) was heated at 100°C with the anhydride (30–50 mmol), zeolite H- β (1.50–2.50 g) (aryl ether: anhydride: zeolite = 10 mmol: 10 mmol: 0.5 g) for 3 h without solvent.

^bThe product was isolated by short path distillation under reduced pressure to determine the yield.

reactions of diphenyl ether or in the reactions of trimethylacetic anhydride could be obtained by conducting those reactions at higher temperatures or for longer periods.

In order to establish whether the zeolite could be reused, a sample of the solid was recovered after reaction and regenerated by heating in air for 3 h at 550°C. It was then reused in an identical reaction of anisole with acetic anhydride (Table 6). The process was repeated a further two times, and the regenerated zeolite retained its full activity even in its fourth use. It is possible, therefore, that a continuous process could be utilized (compare Ref. [30]), although

Table 6
Investigation of the reuse of H- β for reaction according to Eq. (1)^a

Number of previous uses of the zeolite	Yield (isolated, %) of <i>p</i> -methoxyacetophenone
0 (Fresh)	86
1	90
2	87
3	86

^aAnisole (30 mmol), acetic anhydride (36 mmol), zeolite H- β (0.90 g), 120°C, 2 h. The washed and dried zeolite H- β was regenerated in air at 550°C for 3 h prior to each reuse.

we have not attempted to carry out the reaction in this way.

3. Conclusions

H- β zeolite is an efficient catalyst for the acylation of anisole, phenetole and diphenyl ether with unhindered acid anhydrides under modest conditions in the absence of any solvent. This has allowed the development of an effective general procedure for the preparation of aromatic ketones in good yields and with essentially 100% selectivity for the *para*-isomer. The zeolite can be recovered and easily regenerated to render the process economically attractive. Zeolite HY is also effective as a catalyst but gave a lower yield than zeolite H- β under comparable conditions for the reaction of anisole with acetic anhydride. Several other zeolites also catalyse the reaction to a lesser extent.

4. Experimental

All reactions were carried out in the absence of solvent. ¹H and ¹³C NMR spectra were recorded on a Bruker WM-400 spectrometer, operating at 400 MHz for ¹H and 100 MHz for ¹³C. CDCl₃ was used as solvent and chemical shifts are reported as δ (ppm) from TMS. *J* values are recorded in Hz. IR spectra were obtained on a Perkin-Elmer 1750 Fourier Transform instrument. Mass spectra and accurate mass measurements were made at the EPSRC Mass Spectrometry Centre, University of Wales Swansea, using electron impact (EI) and ammonia chemical ionization (CI) techniques. Melting points were determined on a Griffin melting point apparatus and are uncorrected.

Zeolites were provided by PQ zeolites (now Zeolyst International). They were activated by heating in air at 550°C for 3 h prior to use.

4.1. *p*-Methoxyacetophenone

H- β zeolite (1.5 g) was added to a mixture of anisole (3.30 g, 30 mmol) and acetic anhydride

(3.09 g, 30 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off, and washed with diethyl ether (5 × 20 ml). The filtrate and washings were combined and evaporated on a rotary evaporator, and the residue was distilled under reduced pressure to give colourless crystals (3.42 g, 76%), m.p. 36.5–38.0°C (lit. [31], 37°C); ν_{\max} (KBr)/cm⁻¹ 1669 (C=O); δ_{H} 2.55 (3H, s, COCH₃), 3.86 (3H, s, OCH₃), 6.94 (2H, d, *J* 9, 3-H and 5-H), 7.94 (2H, d, *J* 9, 2-H and 6-H); δ_{C} 26.3 (CH₃CO); 55.5 (OCH₃), 113.7 (C-3 and C-5), 130.3 (C-1), 130.6 (C-2 and C-6), 163.5 (C-4), 196.8 (C=O); *m/z* (EI) 150 (M⁺, 30%), 135 (100), 107 (17), 92 (15), 77 (21) and 64 (10).

4.2. *p*-Methoxypropiofenone

H-β zeolite (1.5 g) was added to a mixture of anisole (3.30 g, 30 mmol) and propionic anhydride (4.02 g, 30 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off, washed with diethyl ether (5 × 20 ml) and evaporated. The residue was distilled under reduced pressure to give colourless crystals (3.57 g, 73%), m.p. 27–29°C (lit. [31], 28°C); ν_{\max} (KBr)/cm⁻¹ 1681 (C=O); δ_{H} 1.20 (3H, t, *J* 7, CH₃CH₂CO), 2.93 (2H, q, *J* 7, COCH₂), 3.84 (3H, s, OCH₃), 6.92 (2H, d, *J* 9, 3-H and 5-H), 7.95 (2H, d, *J* 9, 2-H and 6-H); δ_{C} 8.4 (CH₃CH₂), 31.4 (CH₂), 55.4 (OCH₃), 113.7 (C-3 and C-5), 130.1 (C-1), 130.2 (C-2 and C-6), 163.3 (C-4), 199.5 (C=O); *m/z* (EI) 164 (M⁺, 14%), 135 (100), 107 (15), 92 (24), 77 (35), 64 (11).

4.3. *p*-Methoxyisobutyrophenone

H-β zeolite (1.0 g) was added to a mixture of anisole (2.20 g, 20 mmol) and isobutyric anhydride (3.26 g, 20 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 × 15 ml). The combined filtrate and washings were evaporated and the residue was subjected to short path distillation (100–105°C/0.2 mmHg) to

give a colourless liquid (2.603 g, 73%); ν_{\max} (film)/cm⁻¹ 1672 (C=O); δ_{H} 1.20 (6H, d, *J* 7, CH₃CHCH₃), 3.52 (1H, septet, *J* 7, COCH), 3.86 (3H, s, OCH₃), 6.94 (2H, d, *J* 9, 3-H and 5-H), 7.96 (2H, d, *J* 9, 2-H and 6-H); δ_{C} 19.3 ((CH₃)₂), 34.9 (CH), 55.4 (OCH₃), 113.7 (C-3 and C-5), 129.1 (C-1), 130.6 (C-2 and C-6), 163.3 (C-4), 203.1 (C=O); *m/z* (EI) 178 (M⁺, 7%), 135 (100), 107 (11), 92 (17), 77 (22), 64 (6).

4.4. *p*-Methoxy-2,2,2-trimethylacetophenone

H-β zeolite (1.0 g) was added to a mixture of anisole (2.20 g, 20 mmol) and trimethylacetic anhydride (3.76 g, 20 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off, and washed with diethyl ether (5 × 15 ml). The combined filtrate and washings were evaporated. The residue was subjected to short path distillation (103°C/1.0 mmHg) to give a pale brown liquid (0.371 g, 10%); single peak by GC; ν_{\max} (film)/cm⁻¹ 1667 (C=O); δ_{H} 1.37 (9H, s, COC(CH₃)₃), 3.85 (3H, s, OCH₃), 6.90 (2H, d, *J* 9, 3-H and 5-H), 7.86 (2H, d, *J* 9, 2-H and 6-H); δ_{C} 28.4 ((CH₃)₃), 43.9 (C(CH₃)₃), 55.3 (OCH₃), 113.2 (C-3 and C-5), 130.0 (C-1), 130.9 (C-2 and C-6), 162.0 (C-4), 206.3 (C=O); *m/z* (EI) 192 (M⁺, 2%), 135 (100), 107 (10), 92 (13), 77 (21), 64 (10), 57 (7); *m/z* (CI) 193 [(M + 1)⁺, 100%] (HRMS found: 193.1229; calculated for C₁₂H₁₇O₂ 193.1228).

4.5. *p*-Ethoxyacetophenone

H-β zeolite (1.5 g) was added to a mixture of phenetole (3.69 g, 30 mmol) and acetic anhydride (3.09 g, 30 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 × 20 ml). The combined filtrate and washings were evaporated and the residue was distilled under reduced pressure to give colourless crystals (3.78 g, 77%); m.p. 37–38°C (lit. [31], 38°C); ν_{\max} (KBr)/cm⁻¹ 1677 (C=O); δ_{H} 1.44 (3H, t, *J* 7,

$\text{C}_6\text{H}_5\text{CH}_2$), 2.55 (3H, s, COCH_3), 4.09 (2H, q, J 7, OCH_2), 6.91 (2H, d, J 9, 3-H and 5-H), 7.92 (2H, d, J 9, 2-H and 6-H); δ_{c} 14.7 ($\text{CH}_3\text{CH}_2\text{O}$), 26.3 (CH_3CO), 63.7 (OCH_2), 114.1 (C-3 and C-5), 130.1 (C-1), 130.6 (C-2 and C-6), 162.9 (C-4), 196.8 (C=O); m/z (EI) 164 (M^+ , 27%), 149 (47), 121 (100), 107 (4), 93 (28), 77 (9), 65 (14).

4.6. *p*-Ethoxypropiofenone

H- β zeolite (1.5 g) was added to a mixture of phenetole (3.69 g, 30 mmol) and propionic anhydride (4.02 g, 30 mmol) and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 \times 20 ml). The filtrate and washings were combined and evaporated and the residue was distilled under reduced pressure to give colourless crystals (3.95 g, 74%), m.p. 32–33°C; ν_{max} (KBr)/ cm^{-1} 1679 (C=O); δ_{H} 1.21 (3H, t, J 7, $\text{CH}_3\text{CH}_2\text{CO}$), 1.43 (3H, t, J 7, $\text{CH}_3\text{CH}_2\text{O}$), 2.94 (2H, q, J 7, COCH_2), 4.08 (2H, q, J 7, OCH_2), 6.91 (2H, d, J 9, 3-H and 5-H), 7.94 (2H, d, J 9, 2-H and 6-H); δ_{c} 8.5 ($\text{CH}_3\text{CH}_2\text{CO}$), 14.7 ($\text{CH}_3\text{CH}_2\text{O}$), 31.4 (COCH_2), 63.7 (OCH_2), 114.1 (C-3 and C-5), 129.8 (C-1), 130.2 (C-2 and C-6), 162.7 (C-4), 199.5 (C=O); m/z (EI) 178 (M^+ , 29%), 149 (100), 121 (100), 93 (31), 77 (8), 65 (28), 57 (6); (HRMS for M^+ found: 178.0994; calculated for $\text{C}_{11}\text{H}_{14}\text{O}_2$ 178.0994).

4.7. *p*-Ethoxyisobutyrophenone

H- β zeolite (1.0 g) was added to a mixture of phenetole (2.46 g, 20 mmol) and isobutyric anhydride (3.26 g, 20 mmol) and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 \times 15 ml). The filtrate and washings were evaporated and the residue was distilled under reduced pressure to give colourless crystals (2.872 g, 75%), m.p. 38–39°C; ν_{max} (KBr)/ cm^{-1} 1667 (C=O); δ_{H} 1.20 (6H, d, J 7, $(\text{CH}_3)_2\text{CHCO}$), 1.43 (3H, t, J 7, $\text{CH}_3\text{CH}_2\text{O}$), 3.52 (1H, septet, J 7, COCH), 4.09 (2H, q, J 7, OCH_2), 6.92

(2H, d, J 9, 3-H and 5-H), 7.94 (2H, d, J 9, 2-H and 6-H); δ_{c} 14.7 ($\text{CH}(\text{CH}_3)_2$), 19.3 (OCH_2CH_3), 34.9 (CH), 63.7 (OCH_2), 114.2 (C-3 and C-5), 128.9 (C-1), 130.6 (C-2 and C-6), 162.7 (C-4), 203.1 (C=O); m/z (EI) 192 (M^+ , 6%), 149 (100), 121 (95), 93 (19), 65 (20); (HRMS for M^+ found: 192.1150; calculated for $\text{C}_{12}\text{H}_{16}\text{O}_2$ 192.1150).

4.8. *p*-Ethoxy-2,2,2-trimethylacetophenone

H- β zeolite (1.0 g) was added to a mixture of phenetole (2.46 g, 20 mmol) and trimethylacetic anhydride (3.76 g, 20 mmol) and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 \times 15 ml). The filtrate and washings were evaporated and subjected to short path distillation (103°C/0.2 mm Hg) to give a pale brown liquid (0.576 g, 14%); single peak by GC; ν_{max} (film)/ cm^{-1} 1667 (C=O); δ_{H} 1.37 (9H, s, $\text{C}(\text{CH}_3)_3$), 1.43 (3H, t, J 7, CH_3CH_2), 4.08 (2H, q, J 7, OCH_2), 6.88 (2H, d, J 9, 3-H and 5-H), 7.84 (2H, d, J 9, 2-H and 6-H); δ_{c} 14.7 ($\text{C}(\text{CH}_3)_3$), 28.4 (CH_2CH_3), 43.8 ($\text{C}(\text{CH}_3)_3$), 63.6 (CH_2), 13.7 (C-3 and C-5), 129.8 (C-1), 131.0 (C-2 and C-6), 161.4 (C-4), 206.2 (C=O); m/z (EI) 206 (M^+ , 2%), 149 (100), 121 (75), 93 (23), 65 (19), 57 (6); m/z (CI) 207 [($\text{M} + 1$) $^+$, 100%] (HRMS found: 207.1385; calculated for $\text{C}_{13}\text{H}_{19}\text{O}_2$ 207.1385).

4.9. *p*-Phenoxyacetophenone

H- β zeolite (1.0 g) was added to a mixture of diphenyl ether (3.44 g, 20 mmol) and acetic anhydride (2.06 g, 20 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 \times 15 ml). The filtrate and washings were evaporated and the residue was distilled under reduced pressure to give colourless crystals (2.198 g, 52%), m.p. 49.5–50.5°C (lit. [31], 51°C); ν_{max} (KBr)/ cm^{-1} 1679 (C=O); δ_{H} 2.56 (3H, s, CH_3CO), 6.99 (2H, d, J 9, 3-H and 5-H), 7.06 (2H, m, *o*-Ph), 7.19 (1H, m, *p*-Ph), 7.40 (2H,

m, *m*-Ph), 7.93 (2H, d, *J* 9, 2-H and 6-H); δ_c 26.4 (CH₃), 117.3 (*o*-Ph), 120.2 (C-3 and C-5), 124.6 (*p*-Ph), 130.1 (*m*-Ph), 130.6 (C-2 and C-6), 131.8 (C-1), 155.4 (*ipso*-Ph), 162.0 (C-4), 196.7 (C=O); *m/z* (EI) 212 (M⁺, 34%), 197 (100), 141 (25), 135 (8) 115 (29), 77 (48), 63 (11), 51 (22).

4.10. *p*-Phenoxypropiofenone

H- β zeolite (1.0 g) was added to a mixture of diphenyl ether (3.44 g, 20 mmol) and propionic anhydride (2.68 g, 20 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 × 15 ml). The filtrate and washings were evaporated and the residue was distilled under reduced pressure to give colourless crystals (1.937 g, 43%), m.p. 41°C (lit. [32], 38°C); ν_{\max} (KBr)/cm⁻¹ 1678 (C=O); δ_H 1.21 (3H, t, *J* 7.3, CH₃CH₂), 2.95 (2H, q, *J* 7.3, CH₂), 6.99 (2 H, d, *J* 9, 3-H and 5-H), 7.06 (2H, m, *o*-Ph), 7.19 (1H, m, *p*-Ph), 7.37 (2H, m, *m*-Ph), 7.94 (2H, d, *J* 9, 2-H and 6-H); δ_c 8.4 (CH₃), 31.6 (CH₂), 117.3 (*o*-Ph), 120.1 (C-3 and C-5), 124.5 (*p*-Ph), 130.0 (*m*-Ph), 130.2 (C-2 and C-6), 131.6 (C-1), 155.5 (*ipso*-Ph), 161.8 (C-4), 199.4 (C=O); *m/z* 226 (M⁺, 14%), 197 (100), 149 (14), 141 (25), 115 (33), 92 (9), 77 (41), 65 (15), 51 (10).

4.11. *p*-Phenoxyisobutyrophenone

H- β zeolite (1.0 g) was added to a mixture of diphenyl ether (3.44 g, 20 mmol) and isobutyric anhydride (3.26 g, 20 mmol), and the mixture was heated at 100°C for 3 h. The zeolite was filtered off and washed with diethyl ether (5 × 15 ml). The filtrate and washings were evaporated and subjected to short path distillation (130–135°C/1.5 mmHg) to give a colourless liquid (1.279 g, 27%); single peak by GC; ν_{\max} (film)/cm⁻¹ 1680 (C=O); δ_H 1.21 (6H, d, *J* 7, CH(CH₃)₂), 3.51 (1H, septet, *J* 7, CH(CH₃)₂), 6.99 (2H, d, *J* 9, 3-H and 5-H),

7.06 (2H, m, *o*-Ph), 7.19 (1H, m, *p*-Ph), 7.38 (2H, m, *m*-Ph), 7.95 (2H, d, *J* 9, 2-H and 6-H); δ_c 19.3 (CH₃), 35.1 (CH), 117.4 (*o*-Ph), 120.1 (C-3 and C-5), 124.6 (*p*-Ph), 130.0 (*m*-Ph), 130.6 (C-2 and C-6), 130.7 (C-1), 155.5 (*ipso*-Ph), 161.7 (C-4), 203.1 (C=O); *m/z* (EI) 240 (M⁺, 6%), 197 (100), 141 (17), 115 (25), 77 (43), 63 (12), 51 (23); *m/z* (CI) 241 [(M + 1)⁺, 100%]; (HRMS found: 241.1229; calculated for C₁₆H₁₇O₂ 241.1228).

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References

- [1] G.A. Olah, Friedel-Crafts Chemistry, Wiley-Interscience, New York, 1973.
- [2] C.R. Noller, R. Adams, J. Am. Chem. Soc. 46 (1924) 1889.
- [3] P.D. Gardner, J. Am. Chem. Soc. 76 (1954) 4550.
- [4] N.M. Cullinane, S.J. Chard, M. Leyshon, J. Chem. Soc. (1952) 376.
- [5] V. Gold, T. Riley, J. Chem. Soc. (1961) 1676.
- [6] E.J. Bourne, M. Stacey, J.C. Tatlow, J.M. Tedder, J. Chem. Soc. (1951) 718.
- [7] M.S. Newman, J. Am. Chem. Soc. 67 (1945) 345.
- [8] H. Burton, P.F.G. Praill, J. Chem. Soc. (1950) 1203.
- [9] H. Burton, P.F.G. Praill, J. Chem. Soc. (1950) 2034.
- [10] K.B.L. Mathur, J.N. Sharma, K. Venkataraman, H.G. Krishnamurty, J. Am. Chem. Soc. 79 (1957) 3582.
- [11] S. Chodroff, H.C. Klein, J. Am. Chem. Soc. 70 (1948) 1647.
- [12] T. Mukaiyama, T. Ohno, T. Nishimura, S. Suda, S. Kobayashi, Chem. Lett. (1991) 1059.
- [13] K. Suzuki, H. Kitagawa, T. Mukaiyama, Bull. Chem. Soc. Jpn. 66 (1993) 3729.
- [14] K. Smith (Ed.), Solid Supports and Catalysts in Organic Synthesis, Ellis Horwood, Chichester, 1992.
- [15] J.H. Clark, S.R. Cullen, S.J. Barlow, T.W. Bastock, J. Chem. Soc., Perkin Trans. 2 (1994) 1117.
- [16] K. Smith, M. Butters, B. Nay, Synthesis (1985) 1157.
- [17] K. Smith, D. Bahzad, J. Chem. Soc., Chem. Commun. (1996) 467.

- [18] K. Smith, G. Pollaud, J. Chem. Soc. Perkin Trans. 1 (1994) 3519.
- [19] K. Smith, K. Fry, M. Butters, B. Nay, Tetrahedron Lett. 30 (1989) 5333.
- [20] K. Smith, A. Musson, G.A. DeBoos, J. Chem. Soc., Chem. Commun. (1996) 469.
- [21] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille, D. Pioch, J. Org. Chem. 51 (1986) 2128.
- [22] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, Appl. Catal. 30 (1987) 365.
- [23] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Mol. Catal. 50 (1989) 219.
- [24] A. Corma, M.J. Climent, H. Garcia, J. Primo, Appl. Catal. 49 (1989) 109.
- [25] D.E. Akporiaye, K. Daasvatn, J. Solberg, M. Stöcker, Stud. Surf. Sci. Catal. 78 (1993) 521.
- [26] I. Neves, F. Jayat, P. Magnoux, G. Pérot, F.R. Ribeiro, M. Gubelmann, M. Guisnet, J. Mol. Catal. 93 (1994) 169.
- [27] K. Gaare, D.E. Akporiaye, J. Mol. Catal. A 109 (1996) 177.
- [28] Q.L. Wang, Y.D. Ma, X.D. Ji, H. Yan, Q. Qiu, J. Chem. Soc., Chem. Commun. (1995) 2307.
- [29] M. Spagnol, L. Gilbert, R. Jacquot, H. Guillot, P.J. Tirel, A.-M. Le Govic, Proceedings of the Fourth International Symposium on Heterogeneous Catalysis and Fine Chemicals, Basel, Switzerland, September 8–12, 1996.
- [30] P.R. Kurek, US 5,126,489 (1992); Chem. Abstr., 117:150743t.
- [31] C.J. Pouchert, J. Behnke, The Aldrich Library of ^{13}C and ^1H FT NMR Spectra, Aldrich Chemical, 1993, Vol. 2, edn. I.
- [32] N.R. Campbell, F.W. Chattaway, Proc. Roy. Soc., London 130B (1942) 435, Chem. Abstr., 37: 2731⁷.