

Friedel-Crafts Acylation of Aryl-Substituted Carboxylic Acids Catalyzed by Zeolite

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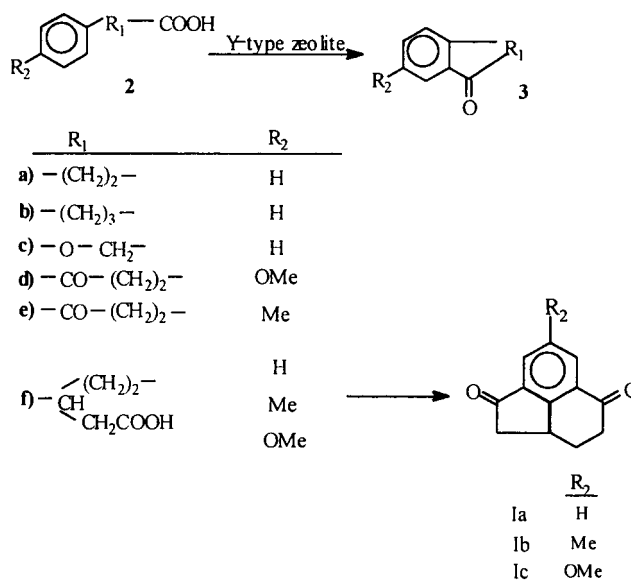
Abstract

A convenient heterogeneous catalytic intramolecular Friedel-Crafts acylation of some aryl-substituted carboxylic acids over Y-faujasite-type zeolite is described. It is an effective method for the synthesis of 4,9-diketo-1,2,3,4-tetrahydroacenaphthenes.

Introduction

As part of a study we sought to use 4,9-diketo-1,2,3,4-tetrahydroacenaphthene **1a** as a precursor in a project aimed to synthesize a few derivatives of partially saturated acenaphthene. To the best of our knowledge, diketone **1a** was previously obtained via acylation of β -phenyladipic acid by PCl_5 in CS_2 in a very poor yield [1]. In order to achieve the synthesis of compound **1a** in a reasonable yield, we tried the acylation reaction by utilizing Lewis acid catalysts (SnCl_4 , TiCl_4 , FeCl_3 , AlCl_3) and protonic acids (polyphosphoric acid, H_2SO_4 , HF), which either were disappointing in accomplishing the desired transformation or gave the expected product (diketone **1a**), after prolong heating and stirring in CS_2 , $\text{C}_6\text{H}_5\text{NO}_2$ and toluene, in poor yield. In another experiment, the reaction was carried out with molten sodium tetrachloroaluminate [2] which afforded about 7–15% of **1a–c**. The reason for the poor yields obtained for diketones **1a–c** by these current methods lies in the fact that these acylating catalysts and some others [3, 4] are excellent for preparation of aryl monoketones (in which the carbonyl group is directly attached to aromatic rings) and usually are not applicable in the synthesis of aryl diketones because the first carbonyl group deactivates the aromatic ring toward further acylation. At this point in order to find an acylating agent to improve the yield of compound **1a**, we turned our attention to the use of zeolites, since recent reports [5–8] showed interesting results on their application in intermolecular FC acylations.

Zeolites, because of their varying acidic and basic properties [9], thermal stability [10] and shape selectivity are important catalysts in a variety of synthetic transformations [11]. Some recent successful examples are: tetrahydropyranylation of alcohols [12], thioacetalization of various carbonyl compounds [13], N-alkylation of aniline derivatives [9] and FC acylations [5–8]. The results of FC reactions



Scheme 1.

showed that zeolites usually gave a much higher ratio of inter- to intra-molecular acylation than Lewis acids such as AlCl_3 [14].

In the present paper we wish to report results of the intra FC acylation of certain aryl-substituted carboxylic acids for the preparation of diketone **1a** and other ketones over a Y-faujasite-type zeolite (Scheme 1).

Experimental

Preparation of CeY-zeolite

The CeY-zeolite was prepared by the following procedure: NaY zeolite (1 g) was added to a molar solution of cerium nitrate (10 mL) and the mixture stirred at ambient temperature

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for 24 h. After filtration the solid CeY-zeolite was washed with distilled water (30 mL) and dried at 100 °C (1.5 h).

General procedure

To a solution of the carboxylic acid (3 mmol) in dry CHCl₃ (40 mL) in a 100-mL round-bottom flask equipped with a condenser and a magnetic stirrer was added CeY-type-zeolite (1.0 g) and the mixture was refluxed for 7–20 h. The progress of the reaction was monitored by TLC. The zeolite was filtered off and the unreacted acid was removed by extraction with NaHCO₃. The organic layer was washed with H₂O (2 × 10 mL) and dried over anhydrous Na₂SO₄. Filtration and evaporation of solvent afforded the corresponded ketone, which was further purified by column chromatography. The zeolite was removed unchanged and reactivated for reuse by washing and heating at 500 °C in the presence of air.

Preparation of diketone **1a**

A mixture of β -phenyl adipic acid (0.666 g, 3 mmol) and CeY-zeolite (1.0 g) with dried CHCl₃ (45 mL) were brought to reflux for 12 h. The reaction mixture was then kept at ambient temperature overnight. The zeolite was filtered off and the unreacted acid was removed by extraction with NaHCO₃ solution. The organic layer was washed with H₂O (2 × 10 mL) and dried over anhydrous Na₂SO₄. Filtration and evaporation of solvent afforded diketone **1a**, which was further purified by column chromatography. Yield 54%.

Characterization of the products

Starting materials were either purchased commercially or prepared in our laboratory by standard methods. The NaY-faujasite-type zeolite was prepared and converted to CeY-zeolite by conventional ion exchange (24 h-room temp.) of NaY with 1 M aqueous Ce(NO₃)₃ solutions. The solid was then thoroughly washed and dried at 80 °C [5]. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advance DPX-250 Spectrometer (in CDCl₃ sol.). IR spectra were recorded on a Shimadzu 470 Spectrophotometer (4000–400 cm⁻¹ region). Mass spectra were obtained on a Shimadzu Spectrometer Model GCMS-QP 1000EX operating under EI conditions (70 eV). The C,H analysis were performed by the microanalytical service of the Research Institute of Petroleum Industry (N.I.O.C). Melting points were measured on a Mettler FP5 apparatus.

Spectroscopic data for (**1a–c**): **1a**: IR (KBr): $\nu(\text{CO}) = 1706$ and 1747 cm^{-1} , ¹H NMR (250 MHz, CDCl₃): $\delta = 7.6$ (q, 1H, J = 2.5 Hz), 7.5 (q, 1H, J = 2.5 Hz), 7.25 (t, 1H, J = 7.5 Hz), 4.15 (m, 2H), 3.6 (m, 1H), 3.1 (m, 2H), 2.9 (q, 2H). ¹³C NMR (250 MHz, CDCl₃): $\delta = 208.82$ (CO), 203.85 (CO), 147.59, 136.31, 133.87, 130.12, 127.87, 127.44, 43.21, 38.14, 34.47, 28.89. MS m/e 186 (M⁺). Anal. Calcd. For C₁₂H₁₀O₂: (C: 77.42, H: 5.38) Found: (C: 77.38, H: 5.36).

1b: IR(KBr): $\nu(\text{CO}) = 1745$, 1705 cm^{-1} , ¹H NMR (CDCl₃): $\delta = 7.4$ (s, 1H), 7.25 (s, 1H), 3.85 (m, 2H), 3.4

Table 1. Acylation of aryl-substituted carboxylic acids with Y-faujasite-type zeolite

Acylyating agent	Product ^b	Time (h)	Yield ^c of 3 (%)	Mp (°C) or bp (°C) ^d	Lit. mp (°C) or bp(°C)
2a	3a	9	20	39–40	40–42
2b	3b	7	25	115–118	113–116
2c	3c	7	30	99–102	102–103
2d	3d	20	Trace	–	–
2e	3e	20	7	88–90	90–91
2f	1a	12	54	146–147	149
	1b	7	61	150–151	–
	1c	7	72	163–164	–

^a All acids prepared by standard methods.

^b All products were characterized by their IR, ¹H NMR and for (**1a–c**) also by ¹³C NMR.

^c Unoptimized yield of isolated pure products.

^d Uncorrected melting or boiling points.

(m, 1H), 2.8 (m, 2H), 2.6 (m, 2H), 2.3 (s, 3H). ¹³C NMR (CDCl₃): $\delta = 207.37$ (CO), 203.04 (CO), 147.11, 135.23, 133.27, 129.15, 127.01, 127.11, 42.32, 37.35, 34.12, 29.11, 27.40. MS m/e 200 (M⁺). Anal. Calcd. for C₁₃H₁₂O₂: (C: 78.00%, H: 6.00%) Found: C: 77.43%, H: 5.84).

1c: IR(KBr): $\nu(\text{CO}) = 1740$, 1701 cm^{-1} , ¹H NMR (CDCl₃): $\delta = 7.2$ (s, 1H), 7 (s, 1H), 3.8 (s, 3H), 3.55 (m, 2H), 2.8 (m, 2H), 2.65 (m, 1H), 2.32 (m, 2H). ¹³C NMR (CDCl₃): $\delta = 204.12$ (CO), 201.73 (CO), 146.40, 135.18, 133.17, 128.78, 116.23, 109.38, 54.23, 45.12, 38.18, 34.03, 27.31. MS m/e 216 (M⁺). Anal. Calcd. for C₁₃H₁₂O₃: (C: 72.22%, H: 5.56%) Found: (C: 71.83%, H: 5.51%).

Results and discussion

The scope of the intramolecular FC acylation is illustrated in Table 1. When treated in the presence of CeY-zeolite in refluxing CHCl₃, monobasic carboxylic acids **2a–c** (Scheme 1) were acylated in low yields to the corresponding cyclic ketones **3a–c** (entries **2a–c**). A similar reaction of β -benzoylpropionic acid and its 4-methyl and 4-methoxy derivatives (**2d–e**) afforded poor yields of cyclic ketones **3d–e**. The poor yields of FC acylation of these acids is attributed to the electron-withdrawing effect of the carbonyl groups on the rings, which deactivate the aromatic ring for electrophilic reaction. Similar treatment of the dibasic carboxylic acids, β -phenyladipic acid and its 4-methyl and 4-methoxy derivatives, with CeY-zeolite in refluxing CHCl₃ for appropriate times leads cleanly to the tricyclic diketones **1a–c** in 54–72% yields. These observations, as previously reported [5], clearly indicate that the size of the acid molecule has a significant role in the acylation process, the yield increases as the size of the acylating molecule increases. A maximum yield (72%) was obtained with β -(4-methoxy)adipic acid.

Conclusion

The present method has the following advantages: The procedure is simple, the conditions are mild and it is an-

other convenient heterogeneous catalytic method for the intramolecular acylation of carboxylic acids without a need to use a flow reactor or an autoclave and conducted at high temperature which is common in most procedures using zeolites. Also it is noteworthy that this procedure could be unique in the preparation of aryl diketones (such as **1a**) directly and in one step.

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References

1. R.H. Manske: *J. Am. Chem. Soc.* **53**, 1104 (1931).
2. L.G. Wade, K.J. Acker and R.A. Osteryoung: *J. Org. Chem.* **44**, 3724 (1979).
3. J.B. Hendrickson and S.M. Hussoin: *J. Org. Chem.* **54**, 1144 (1989).
4. V. Premasagar, A.V. Palaniswamy and J.E. Eiesenbraun: *J. Org. Chem.* **46**, 2974 (1981).
5. B. Chiche, A. Finiels, C. Gauthier and P. Geneste: *J. Org. Chem.* **51**, 2128 (1986).
6. R. Sreekumar and R. Padamakumar: *Synth. Commun.* **27**, 777 (1997).
7. B. Chiche, A. Finiels, C. Gauthier and P. Geneste: *Appl. Catal.* **30**, 365 (1987).
8. C. Gauthier, B. Chiche, A. Finiels and P. Geneste: *J. Mol. Catal.* **50**, 219 (1989).
9. M. Onaka, A. Omezono, M. Kawai and Y. Izumi: *J. Chem. Soc. Chem. Commun.* 1202 (1985).
10. P.R. Townsend: *The Properties and Application of Zeolites*; Special Publication No. 33, The Chemical Society, London (1980).
11. W. Holderich, M. Hesse and F. Newmann: *Angew. Chem.* **100**, 232 (1988); *Angew. Chem. Int. Ed. Engl.* **27**, 226 (1988).
12. P. Kumar, C.U. Dinesh, R.S. Reddy and B. Pandey: *Synthesis* 1069 (1993).
13. P. Kumar, R.S. Reddy, A.P. Singh and B. Pandey: *Synthesis* 67 (1993).
14. A. Corma, M.J. Climate, H. Garcia and J. Primo: *J. Appl. Catal.* **49**, 109 (1989).

