Pergamon

Tetrahedron Letters 42 (2001) 1163–1165

TETRAHEDRON
LETTERS

A mild procedure for rapid and selective deprotection of aryl acetates using natural kaolinitic clay as a reusable catalyst

B. P. Bandgar,* L. S. Uppalla, A. D. Sagar and V. S. Sadavarte

Organic Chemistry Research Laboratory, School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431 606, India

Received 25 August 2000; revised 15 November 2000; accepted 29 November 2000

Abstract—A variety of aryl acetates are selectively cleaved to the corresponding phenols using natural kaolinitic clay in methanol under mild conditions (25°C). © 2001 Published by Elsevier Science Ltd.

Phenolic hydroxyl groups occur widely in plant and animal life, both land-based and aquatic, as demonstrated by the vast number of natural products that contain this group.[1] In developing a synthesis of any phenol-containing product, protection is often mandatory to prevent reaction with oxidizing agents and electrophiles or reaction of the nucleophilic phenoxide ion with even mild alkylating and acylating agents. The protection of phenols as *O*-acyl derivatives has long played a key role in organic synthesis, because of the ease with which they are formed and cleaved. In spite of several efforts, the methods available for selective removal of aryl acetates in the presence of other sensitive functional groups are very few,[2] not general[3] and most involve homogenous conditions. The recently reported ytterbium triflate,[4] unlike hafnium triflate,[5] cleaves aryl acetates without Fries migration. However, it requires long reaction times, drastic conditions, aqueous work-up and does not discriminate between aryl and alkyl acetates. Recently, there has been an upsurge in the application of clay as a catalyst for organic reactions.[6] In continuation with our ongoing research in this area,[6c,d] we wish to report in this communication a preliminary account of use of natural kaolinitic clay (N.C.) as a catalyst for the selective removal of aryl acetates in the presence of other sensitive functional groups under mild conditions (Scheme 1).

Natural kaolinitic clay was obtained from the Padappakara mine of Quilon District, Kerala, India and it was purified and supplied by Dr. Lalithambika, RRL, Trivandrum, and it was used as obtained without any pretreatment.

A series of aryl acetates were subjected to the deprotection conditions with natural kaolinitic clay catalyst in methanol at 25°C to obtain the corresponding phenols. The results are presented in Table 1. It is important to note that this environmentally benign and manipulatively simple protocol allows chemoselective deprotection of aryl acetates in the presence of several other protecting groups, such as oximes (entry 3), THP ethers (entry 8), thioacetals (entry 9), NH-acetyl (entries 10 and 14), and *t*-butoxycarbonyl groups[6a] (entry 15). Functional groups, such as aldehydes (entries 2 and 6), imines (entry 4), and benzoates (entry 17), remain unaltered under these reaction conditions. Furthermore, it is notable that aryl acetate groups are removed selectively in the presence of benzyl acetates (entries 7, 12, and 13). No deacylation was observed for alkyl acetates (entries 14, 15, and 18) and phenyl thioacetate (entry 16). An important feature of this method is that the optical purities of the products (entries 13–15) remain unaltered (based on optical rotation). The present reaction conditions allow exclusive aryl deacetylation with no trace of Fries migration products. The tolerance of different protecting groups to these reaction conditions illustrates the flexibility and generality of the protocol.

In conclusion, the present results demonstrate the novelty of natural kaolinitic clay that shows unique selec-

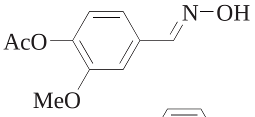
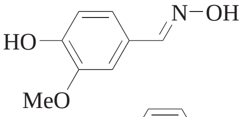
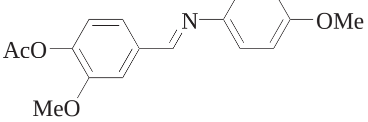
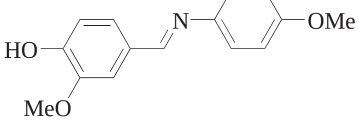
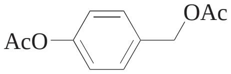
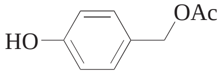
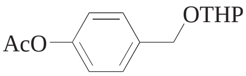
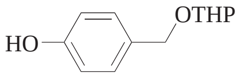
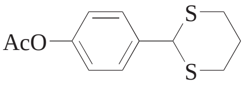
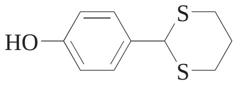
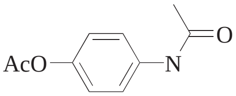
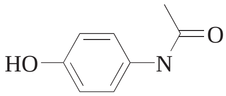
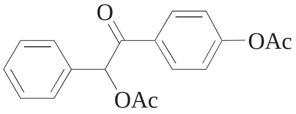
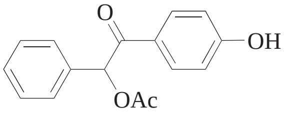
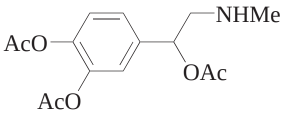
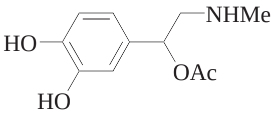
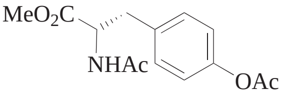
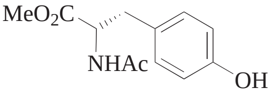
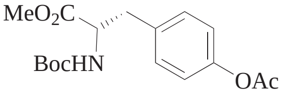
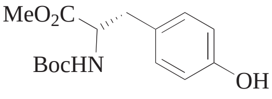
Scheme 1.

Keywords: catalyst; aryl acetates; deprotection; phenols.

* Corresponding author. Fax: 0091-2462-29245; e-mail: upekam@hotmail.com

0040-4039/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0040-4039(00)02198-5

Table 1. Deprotection of aryl acetates using natural kaolinitic clay under mild conditions

Entry	Substrate	Product	Reaction time (min)	Yield %[a,b]
1	Phenyl acetate	Phenol	20	96
2	4-Acetoxy-3-methoxy benzaldehyde	Vaniline	30	90
3			30	91
4			30	89
5	β-Naphthyl acetate	β-Naphthol	20	95
6	4-Acetoxy benzaldehyde	4-Hydroxy benzaldehyde	30	90
7			30	94
8			20	92
9			20	90
10			20	89
11	1,4-Phenylenediacetate	Hydroquinone	20	89
12			20	92
13			30	88 (99% ee)
14			30	93 (99% ee)
15			30	93 (98% ee)
16	Phenyl thioacetate	No reaction	12 h	--
17	4-Benzoyloxy benzaldehyde	No reaction	12 h	--
18	$CH_3(CH_2)_4COOCH_3$	No reaction	12 h	--

[a] Yield of pure isolated products. [b] Products characterized by spectral analysis and physical properties.

tivity and constitutes a useful alternative to commonly accepted deacylation procedures. Moreover, the superiority and flexibility of the protocol lies in its ease of operation and simplicity in work-up, which involves mere filtration of the catalyst that can be reused at least three times without appreciable loss of activity.

General procedure:

The aryl acetate (5 mmol) and natural clay (100 mg) were stirred in methanol (10 ml) at 25°C. After completion of the reaction (TLC), the catalyst was filtered off and washed with ethyl acetate (2×5 ml). The solvent was removed under vacuum to furnish the phenol in almost pure form, which was further purified by column chromatography on SiO_2 (hexane:ethyl acetate = 9:1) where necessary.

Acknowledgements

V.S.S. thanks CSIR, New Delhi for the Junior Research Fellowship and we thank Dr. Lalithambika, RRL, Trivandrum for the supply of natural clay.

References

1. Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991.
2. Chakrabarti, A. K.; Nayak, M. K.; Sharma, L. *J. Org. Chem.* **1999**, *64*, 8027 and references cited therein.
3. Baptistella, L. H. B.; dos Santos, J. F.; Ballabio, K. C.; Marsaioli, A. J. *Synthesis* **1989**, 436 and references cited therein.
4. Sharma, G. V. M.; Ilangovan, A. *Synlett* **1999**, *12*, 1963.
5. Kobayashi, S.; Moriwaki, M.; Hichiya, I. *Tetrahedron Lett.* **1996**, *37*, 2053.
6. (a) Shaikh, N. S.; Gajre, A. S.; Deshpande, V. H.; Bedekar, A. V. *Tetrahedron Lett.* **2000**, *41*, 385; (b) Cornelis, A.; Laszlo, P. *Synlett* **1994**, 155; (c) Bandgar, B. P.; Uppalla, L. S.; Kurule, D. S. *Green Chem.* **1999**, 243; (d) Bandgar, B. P.; Kasture, S. P. *Green Chem.* **2000**, *2*, 154.