



ELSEVIER

Journal of Molecular Catalysis A: Chemical 104 (1995) L127–L129



Letter

Aromatic substitution reactions of benzyl derivatives with a bentonite clay

Manuel Salmón ^{a,*}, Nieves Zavala ^a, Armando Cabrera ^a, Jorge Cárdenas ^a,
Rubén Gaviño ^a, René Miranda ^b, Mariano Martínez ^{*,a}

^a Instituto de Química de la Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria Coyoacán 04510, México D.F., Mexico

^b Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, Cuautitlán Izcalli, Estado de México, México

Received 16 December 1994; accepted 16 May 1995

Abstract

Two examples of catalytic induction with a bentonite clay to form phenylmethanes and aromatic ethers from benzyl derivatives are discussed.

Keywords: Bentonite clay; Benzyl ethers; Oligomerization; Phenylmethanes

1. Introduction

Bentonites (montmorillonites), among other layer silicates, are powerful catalysts for a wide range of chemical processes, particularly those requiring the intermediacy of protonated species. Montmorillonites have been shown to be efficient heterogeneous catalysts to generate a number of novel organic reactions under mild conditions, providing high selectivity and good yields [1].

This particular class of catalysts has been found to show versatile Lewis–Brønsted properties [2] inducing aromatic substitutions involving benzylic carbocation species [3,4]. They have considerable advantages over conventional homogeneous acid catalysts. The products can be obtained after simple removal of the catalyst by filtration or centrifugation. Conversely, the con-

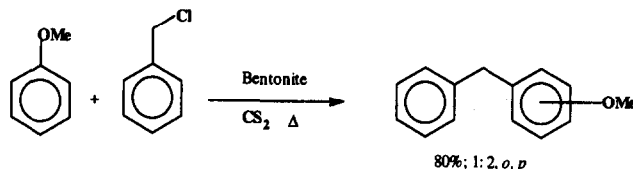
ventional aromatic electrophilic substitution performed through the Friedel–Crafts reaction using common Lewis acids, such as anhydrous AlCl₃, FeCl₃, etc., generally gives complex reaction mixtures which require an intricate and laborious work-up to isolate the products [5].

2. Results and discussion

In order to determine the potential of the bentonite clay¹, we have examined the alkylation of

¹ *Bentonite clay.* – On examination by X-ray fluorescence, the montmorillonite type clay employed in this study proved to have the following composition (in %): SiO₂, 75.4; Al₂O₃, 9.3; MgO, 0.4; Fe₂O₃, 1.3; CaO, 4.0; K₂O, 0.4; TiO₂, 0.4; H₂O(110°) 9.5. The commercial acid-activated material was obtained from Tonsil Mexicana and analyzed with a Philips spectrometer using Cr primary radiation. The measured specific surface area was 307 m²/g (BET N₂) and the pore volume was 0.4789 cm³/g. The acidity by NH₃ thermodesorption was 0.099 mequiv./g. The particle size was 325 mesh.

* Corresponding author. Fax: (+52-5)6162203.



Scheme 1.

anisole by benzyl chloride and the reaction with *para*-methoxybenzyl alcohol. From the isolated products, it was deduced that diverse organic reactions, unusual in solution chemistry, take place over layer silicates. This might be due to the protonated and unprotonated surface active sites in the micro-environment which facilitate intermolecular reactions.

In a first example, anisole (3.24 g, 0.03 mol) and benzylchloride (3.8 g, 0.03 mol) were dissolved in CS₂ (10 ml) and refluxed with a bentonite clay suspension (0.15 g) for 4 h. The reaction mixture was allowed to stand at room temperature. The mixture was filtered over Celite and the filtrate concentrated under reduced pressure. The residue was purified by column chromatography using SiO₂ eluted with *n*-hexane/CH₂Cl₂ (98:2). Pure *ortho*- and *para*-methoxyphenylmethanes (Scheme 1) were obtained in 80% yield in a 1:2 ratio and characterized by spectroscopic means². This reaction clearly follows an aromatic electrophilic substitution mechanism.

In a second example, *para*-methoxybenzyl alcohol **1** (5.0 g, 0.046 mol) was condensed on 0.5 g bentonite using the same conditions as those described elsewhere [6]. The reaction afforded bis(4-methoxyphenyl)methane **2**, bis(4-methoxybenzyl) ether **3**, bis-(4-methoxybenzyl)

acetal **4** and [3'-(4''-methoxybenzyl)-4'-methoxybenzyl]-[4-methoxybenzyl] ether **5**, as pure compounds with yields of 14, 58, 0.8 and 9.2% respectively, Fig. 1³.

The formation of compound **2** could be explained by an *ipso* attack of **1** to the benzylic cation **6**, yielding the intermediate **7** (Scheme 2), where one formaldehyde molecule is lost.

The presence of free formaldehyde in the reaction medium was confirmed by Schryver's test [7] and by the bis *para*-methoxybenzyl acetal isolation **4** synthesized by Cornélis and Laszlo [8] (Scheme 3). In the reaction, the bis-*para*-benzyl ether derivative **3** seems to generate other molecules like **5**, where exclusively one phenyl group

³ Their ¹H and ¹³C NMR and other spectroscopic data which confirm the proposed structures are as follows:

Bis-(4-methoxyphenyl) methane **2** was isolated as white crystals (0.7 g, mp 50–51°C), ¹H NMR (CDCl₃, 300 MHz), 7.02 and 6.82 (AA'BB' system, 8H, *J* = 8 Hz), 3.85 (s, 2H), 3.75 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz), 158.5 (s), 134.1 (s), 129.9 (d), 113.8 (d), 55.0 (t), 40.1 (q); MS (70 eV) 228 (M⁺, 100), 213 (16), 198 (12), 197 (84), 166 (5), 121 (48), 91 (30), 77 (40), 63 (20), 51 (22), 39 (19). Bis-(4-methoxybenzyl) ether **3** was isolated as white crystals (2.9 g, mp 39–40°C), ¹H NMR (CDCl₃, 300 MHz), 7.28 and 6.88 (AA'BB' system, 8H, *J* = 8 Hz), 4.46 (s, 4H), 3.81 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz), 159.2 (s), 130.5 (s), 129.4 (d), 113.8 (d), 71.4 (t), 55.3 (q); MS (70 eV) 258 (M⁺, 5), 137 (2), 121 (100), 91 (30), 77 (71), 78 (83), 51 (40), 39 (30). Bis-(4-methoxybenzyl) acetal **4** was isolated as gum (0.04 g), ¹H NMR (CDCl₃, 300 MHz), 7.28 and 6.88 (AA'BB' system, 8H, *J* = 8 Hz), 4.79 (s, 2H), 4.57 (s, 4H), 3.80 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz), 159.2 (s), 129.9 (s), 129.6 (d), 113.8 (d), 93.4 (t), 69.0 (t), 55.2 (q); MS (70 eV) 288 (M⁺, 1), 137 (21), 121 (100), 91 (23), 77 (40). [3'-(4''-Methoxybenzyl)-4'-methoxybenzyl]-[4-methoxybenzyl] ether **5** was isolated as yellow oil (0.46 g), ¹H NMR (CDCl₃, 300 MHz), 7.21 and 6.83 (AA'BB' system, 4H, *J* = 8 Hz), 7.04 (d, 1H, *J* = 2.2 Hz), 7.11 and 6.83 (AA'BB' system, 4H, *J* = 8.6 Hz), 7.11 (dd, 1H, *J* = 8.6, 2.2 Hz), 6.79 (d, 1H, *J* = 8 Hz), 4.39 (s, 2H), 4.38 (s, 2H), 3.90 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz), 159.1 (s), 157.7 (s), 156.8 (s), 132.9 (s), 130.4 (s), 130.0 (d), 129.9 (s), 129.8 (d), 129.4 (s), 129.3 (d), 127.1 (d), 113.6 (d), 113.5 (d), 110.1 (d), 71.3 (t), 71.2 (t), 55.3 (q), 55.1 (q), 34.8 (t); MS (70 eV) 378 (M⁺, 8), 257 (35), 241 (12), 227 (20), 121 (100), 91 (18), 77 (21).

² *ortho*-Benzyl anisole was isolated as a yellow oil (1.74 g), ¹H NMR (CDCl₃, 300 MHz), 7.23 (m, 6H), 7.07 (dd, 1H, *J* = 8, 1 Hz) 6.88 (m, 2H), 4.0 (s, 2H), 3.8 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz), 157.5 (s), 140.5 (s), 130.3 (d), 128.9 (d), 128.3 (d), 127.6 (d), 125.7 (d), 124.8 (s), 120.4 (d), 110.3 (d), 55.1 (q), 36.0 (t); MS (70 eV) 198 (M⁺, 82), 183 (45), 165 (60), 121 (20), 91 (100), 77 (50), 65 (40), 51 (54), 39 (50). *para*-Benzyl anisole was isolated as gum (3.48 g), ¹H NMR (CDCl₃, 300 MHz), 7.22 (m, 4H), 7.11 and 6.78 (AA'BB' system, 4H, *J* = 8 Hz), 7.82 (m, 1H), 3.92 (s, 2H), 3.77 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz), 157.5 (s), 140.5 (s), 130.3 (d), 128.9 (d), 128.3 (d), 127.6 (d), 125.7 (d), 124.8 (s), 120.4 (d), 110.3 (d), 55.2 (q), 36.1 (t); MS (70 eV) 198 (M⁺, 100), 183 (30), 167 (56), 121 (49), 91 (48), 77 (55), 51 (92), 39 (60).

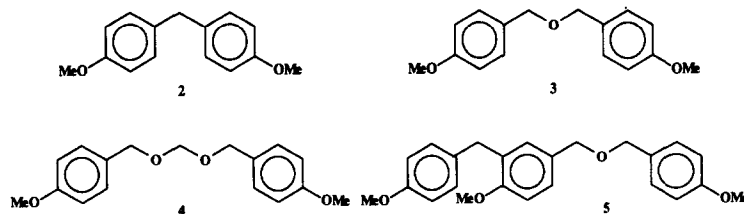
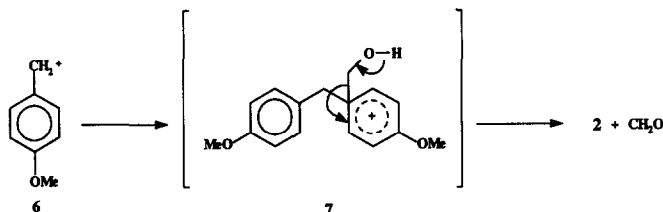
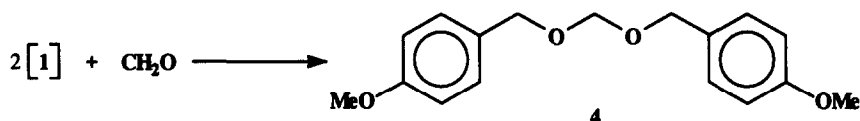


Fig. 1.



Scheme 2.



Scheme 3.

of the ether is mono-, di- or tri-substituted, yielding in some cases cyclic oligomers [6].

From these results, we can infer that the catalytic reaction of benzyl alcohol in the presence of clay is sensitive to the number of methoxy substituents in the aromatic ring. The presence of a methoxy group in *para* position precludes the cyclic oligomerization observed when the 3,4,5-trimethoxybenzyl alcohol was used as substrate [6].

References

- [1] M. Salmón, G. Penieres, R. Miranda and C. Alvarez J. *Heterocyclic Chem.*, 18 (1981) 1475. M. Salmón, R. Miranda and E. Angeles, *Synth. Commun.*, (1986) 1827. A. Cabrera, N. Rosas, C. Márquez and M. Salmón, *Gazz. Chim. Ital.*, 121 (1991) 127. A. Cabrera, C. Márquez, N. Rosas, R. Miranda, E. Angeles and M. Salmón, *Rev. Soc. Quím. Méx.*, 36 (1992) 8. A. Cabrera, D. Vázquez, L. Velasco, M. Salmón and J.L. Arias, *J. Mol. Catal.*, 75, (1992) 101.
- [2] P. Laszlo, *Science*, 235 (1987) 1473.
- [3] M. Salmón, R. Miranda and E. Angeles, *J. Chem. Soc., Chem. Commun.*, (1990) 1188.
- [4] J.A. Ballantine, M. Davies, H. Purnell, M. Rayanakorn, J.M. Thomas and K.J. Williams, *J. Chem. Soc., Chem. Commun.*, (1981) 427. J.A. Ballantine, M. Davies, I. Patel, H. Purnell, M. Rayanakorn, J.K. Williams and J.M. Thomas, *J. Mol. Catal.*, 26 (1984) 37. J.A. Ballantine, J.H. Purnell and J.M. Thomas, *J. Mol. Catal.*, 27 (1984) 157.
- [5] X. Fu, M. He, Q. Lei and B. Luo, *Synth. Commun.*, 21 (1991) 1273.
- [6] M. Salmón, N. Zavala, M. Martínez, R. Miranda, R. Cruz, J. Cárdenas, R. Gaviño and A. Cabrera, *Tetrahedron Lett.*, 35 (1994) 5797.
- [7] J.F. Walter, *Formaldehyde*, Reinhold Publishing Co., New York, 1944.
- [8] A. Cornélis and P. Laszlo *Synthesis*, (1982) 162.