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# One-Pot Synthesis of Phenylmethanes Using $Al^{3+}$ Doped and Natural Clays

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# ONE-POT SYNTHESIS OF PHENYLMETHANES USING $AL^{3+}$ DOPED AND NATURAL CLAYS.

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**Abstract:** New simple alternatives to produce phenylmethanes using toluene and toluene derivatives are reported; such processes are catalyzed by a natural and a doped $Al^{3+}$ Mexican bentonitic earth. The clays show a dual catalytic effect, as inductors of free radicals and as catalysts of electrophilic aromatic substitution. The catalytic effect as well as some physical and chemical properties of the clays are also reported.

## INTRODUCTION

In a recent communication[1] we reported the synthesis of *ortho* and *para*-benzyltoluenes from toluene and bromine by means of a commercial clay[2] as the catalyst, the first known example of two catalytic reactions within one system.

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These phenylmethanes and some of its derivatives have received much attention due to their well known use as constituents of germicidal soaps, bactericides for *tubercle bacilli in vitro* as well as plastizicers.[3-5] Of particular interest is their application as insulating oils in high-voltage electrical devices and as high octane fuels for aircraft engines.[6,7]

Several methods exist to prepare the named compounds, but they rely on Friedel-Crafts reactions between benzylhalides, toluene and $ZnCl_2$ or $AlCl_3$ as the catalyst.[8] Those catalyst however, have severe restriction due to their higher cost.[2] In this view the use of natural and modified clays as the catalystic promotor, represents an important and attractive alternative.

Related with our research program[9] on the use of a Mexican bentonite, in this work we wish to report the results of several experiments performed in order to obtain arylmethanes (**1**-**3**) using the clays under study as the catalytic moiety. In the table we have summarized the results of new simple alternatives to synthesize compounds **1**-**3**. It shows that the target products were obtained generally in good yield.

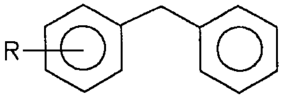
In the course of obtaining molecules **1** and **3** we found that these compounds may be generated at RT by means of the $Al^{3+}$ doped clay; this is in accord with the increase of specific surface area and number of Lewis acid sites for such a clay. In general, the work-up was simple and the crude reaction mixture shows essentially one spot on tlc (*n*-hexane/AcOEt 9:1; $CeSO_4/H_2SO_4$ 1N).

In addition, the clays showed a dual catalytic effect: as free radical promoters (entries 1,2,8) as it was previously demonstrated[1]

Table.- Alternatives to pruduce arylmethanes using $Al^{3+}$ doped and non doped Tonsil Optimum Extra.

| Entry | Clay[a] | Reagents | Temp (°C ) | Time (Hr) | Yield[b] ( % ) | Product[c] |
|---|---|---|---|---|---|---|
| 1 | ND | $C_7H_8$/ $PBr_3$ | 100 | 4 | 50 | **1** |
| 2 | ND | $C_7H_8$/ $PCl_3$ | 100 | 6 | 30 | **1** |
| 3 | ND | $C_7H_8$/ $C_6H_5CH_2OH$ | 100 | 5 | 75 | **1** |
| 4 | ND | $C_7H_8$/ $C_6H_5CH_2Cl$ | 100 | 2 | 90 | **1** |
| 5 | ND | $C_6H_5CH_2OH$ | 100 | 8 | 50 | **2** |
| 6 | ND | $C_6H_6$/ $C_6H_5CH_2Cl$ | 70 | 3 | 90 | **3** |
| 7 | AD | $C_6H_6$/ $C_6H_5CH_2Cl$ | RT | 4 | 80 | **3** |
| 8 | AD | $C_7H_8$/ $Br_2$ | RT | 5 | 80 | **1** |

a) ND = Non doped clay; AD = $Al^{3+}$ doped clay.
b) Yields are of isolated pure compounds.
c) *ortho* and *para* ratio 1:2; for **1** and **2**.



| | | R |
|---|---|---|
| **1** | *o*- and *p*- | Me |
| **2** | *o*- and *p*- | $CH_2$ OH |
| **3** | | H |

and in general (entries **1-8**) as Lewis acid for Friedel-Crafts alkylation. Infrared spectrophotometry, using the pyridine method[10] was employed, in order to determinate the presence of Lewis acid sites (1540 and 1450 $cm^{-1}$). Finally, when the structures of the natural and the modified clays were compared, an important increment in surface area was detected. It went from 55.30 $m^2/g$ in the original clay to 200 $m^2/g$ in the case of the doped clay. According to X-ray diffraction the interlayer distance was also found to have changed, 15 A for the undoped clay and 17.3 A in the modified one.

## EXPERIMENTAL SECTION

Purified molecules were characterized by spectroscopic means. $^1H$ NMR spectra were recorded in a Varian FT-200 spectrometer using $CDCl_3$ as solvent and TMS as internal reference. EIMS (70 ev) spectra were obtained in a Shimadzu GCMS-QP 2000A spectrometer. The natural and the modified clays were originaly obtained from Tonsil Mexicana[2] and analyzed with a SIEMENS D 5000 DIFRACTOMETER using the Cu K $\alpha_1$ radiation. The measured specific surface areas were determinated by BET $N_2$ method. The Lewis character of catalytic species was identified in a Perkin-Elmer 1600 Series FTIR spectrophotometer, according to the pyridine coordination method.

**$Al^{3+}$doped clay[11].-** It was prepared as follows: the clay was suspended in bidestilled water (10 g/l) and cation exchanged with a chlorhydrol (Reheis Co.) of $Al^{3+}$-polyoxication under reflux conditions. Such sample was aged about one week, isolated by filtration and dried at 100 °C, 12 h; finally it was calcinated at 400 °C for 4 h.

**Typical example.-** 0.8 g (5 mmol) of bromine with 50 ml of anhydrous toluene, were magnetically stirred at RT in presence of 100 mg of the $Al^{3+}$ doped clay for 4 h. The transformation was monitored by tlc (*n*-hexane/AcOEt 9:1), and GC-MC for the appearance and disappearance of the reaction intermediate benzylbromide. After disappearence of the intermediate, the reaction mixture was filtered over Celite, washed with $NaHCO_3$ 5% (3x5 ml), then with $H_2O$ (3x5 ml) and dried with $Na_2SO_4$. Finally, the excess of toluene was removed by fractionated destilation and the residue purified by column chromatography. An 80% yield of pure *o*-and *p*-benzyltoluenes **1** (1:2) were obtained.

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