

Letter

In situ free radical and carbocation reactions between alkylbenzenes promoted by a bentonite clay

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Abstract

The reaction between *n*-alkylbenzenes and bromine catalyzed with a bentonitic clay in absence of light, afforded directly substituted phenyl methanes or α -halogenated alkylbenzenes. This one-pot general method, can be used for the preparation of benzylhalides, alkyl substituted or unsubstituted methylene bridge phenyl methanes.

Keywords: Phenyl methanes; Alkylbenzylhalides; Bentonite clay; Free radicals; Aromatic substitution

1. Introduction

The literature abounds in information on the preparation of phenyl methanes. They have important applications in the production of pesticides [1], insulating oils for high-voltage electrical devices [2,3], constituents of germicidal soaps [4], bactericides [5], plasticizers and components in high octane fuels for aircraft engines [3,6].

Benzene, toluene and benzylhalides are the preferred substrates to be condensed by Friedel–Crafts reactions using a large number of different catalysts. The Grignard reaction be-

tween an arylmagnesium halide with benzylaldehydes and the reduction of phenylketones, are other widespread methods used for phenyl methane preparations. However the above reactions require substrates with a functionalized center possessing a labile or active group to perform the aromatic substitution.

An attractive, inexpensive general and useful alternative is to employ natural and Al³⁺ doped modified clays as catalysts to synthesize phenyl methanes directly from alkylbenzenes [7]. Previously we reported the synthesis of *ortho*- and *para*-methyl phenyl methanes from toluene [8]. In this reaction, the methyl group was activated by bromine and a montmorillonite clay, favouring the free radical formation and the aromatic substitution at the same time. This new and unusual reaction, moved us to search on the application of this catalytic method to determine its general use in the synthesis of organic molecules.

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2. Experimental

2.1. Catalyst characterization

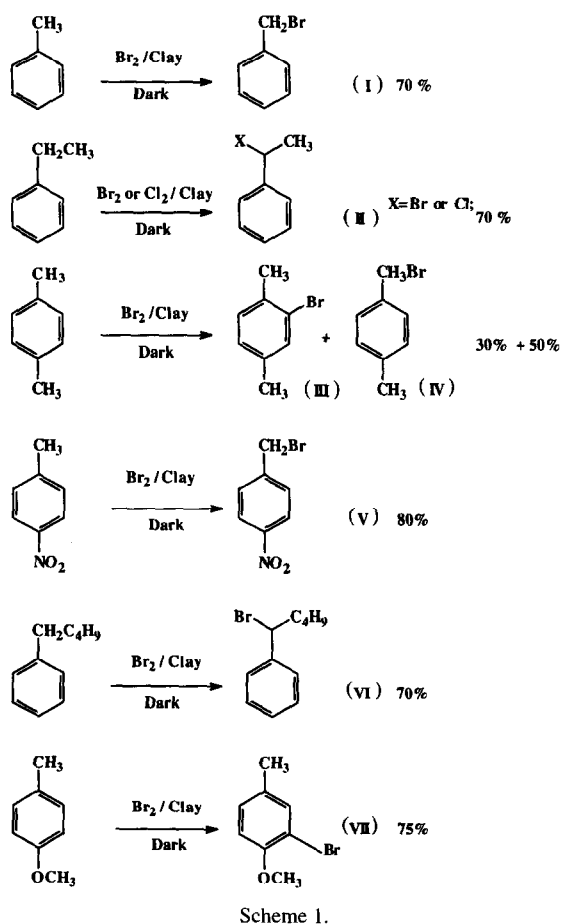
Bentonite clay. On examination by X-ray fluorescence, the montmorillonite type clay employed in this study proved to have the following composition (in %): SiO₂, 75.4; Al₂O₃, 9.3; MgO, 0.4; Fe₂O₃, 1.3; CaO, 4.0; K₂O, 0.4; TiO₂, 0.4; H₂O (110°C) 9.5. The commercial acid-activated material was obtained from Ton-sil 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. The clay was calcined at 400°C during four

hours and stored at 130°C. The pyridine method was used to examine the acidity of the clay coupled with the IR spectrophotometry to measured the chemisorbed base in the region of 1540 and 1450 cm⁻¹ [9]. The interlayer distance of 15 Å was obtained by X-ray diffraction.

2.2. Preparation of benzylhalides and phenyl methanes

A set of examples of the free radical reaction are shown in Scheme 1. The alkylbenzylhalides were prepared from different substrates in reasonable high yields, comparable with those obtained from reported methods which require external energy to promote the halogenation. The isolated products were formed in absence of light at 0°C or at r.t., dropping bromine (0.021 mol) onto a stirred alkylbenzene (0.01 mol) (net) or in CS₂ (20 ml) solution for 2 h containing (0.050 g) of bentonite clay in suspension. The purified products: benzylbromide (I), (1-bromo)ethylbenzene *dl* (II), 2-bromo-*p*-xylene (III), 4-methylbenzylbromide (IV), 4-nitrobenzylbromide (V), 1-bromopentylbromide *dl* (VI) and *p*-methoxy-3-bromotoluene (VII), were characterized by comparison of their ¹H NMR and IR with published spectra or with authentic samples [10].

The phenyl methanes displayed in Scheme 2, were prepared in one step, refluxing the reactions for 2 to 4 h containing the same amount of reagents and catalyst as above. All reactions were performed without light stirring and monitored by SiO₂ TLC. The suspension was allowed to stand at room temperature, filtered over Celite to remove the bentonite and the filtrate concentrated under reduced pressure. The residue was analysed by GCMS and purified by column chromatography using SiO₂ and hexane or hexane/ethyl acetate as eluent to give 70 to 85% yields of the pure compounds. The 2-methyl diphenyl methane (VIIIa) and 4-methyl diphenyl methane (VIIIb) were characterized by comparison of their ¹H NMR, IR and mass



clear that the reactivity of the benzylic hydrogens are affected by the aromatic substituents. The α -halogenation is favoured through a free radical reaction when unsubstituted alkylbenzenes or *para*-nitrotoluene are used as substrates. Whereas when *para*-xylene or *para*-methoxytoluene are brominated, an electrophilic substitution was also observed. The electron-releasing and -withdrawing groups were reported to increase and decrease, respectively, the rate of benzylhalide formation in substituted toluenes towards attack by atomic bromine [14]. Thus, we can conclude that strong electron-withdrawing groups tend to stabilize the benzyl radicals as well as the benzylbromides. Whereas when the aromatic ring is substituted with electron-donating groups, the catalytic clay works to yield free radicals and electrophilic aromatic substitution. Here, it is also worth mentioning that nuclear substitutions have been observed to markedly affect the reactivity of the benzylic hydrogens of alkylbenzenes towards attack by certain free radicals [14].

In this work, the hydrogen abstraction by atomic bromine through free radicals to lead the specific α -bromination of the methyl and *n*-alkylbenzenes, was confirmed when hydroquinone was added to the reaction. The result was a total inhibition of the previously isolated products. The phenyl methanes are formed through a simple one pot synthesis involving firstly the benzylhalide formation via a free radical reaction followed by an electrophilic reaction on the substituted *n*-alkylbenzene.

The catalytic aromatic substitution reaction regiospecifically afforded *para* alkyl phenyl methanes, which are unsymmetrically substituted, when the alkyl substituents are not methyl groups. Cross-over experiments showed that the reaction is intermolecular, probably due to the protonated and unprotonated surface active sites in the micro-environment of the catalyst layers which facilitate the intermolecular reactions [15]. This phenyl methane catalytic synthesis gives a new source with which to prepare complex aromatic compounds.

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