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MONTMORILLONITE K10 CLAY CATALYSED FRIEDEL-CRAFTS ARALKYLATION IN ROOM TEMPERATURE: SYNTHESIS OF FUNCTIONALISED LINEAR ARYL-ALKYL-ARYL SYSTEMS

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Abstract: The Montmorillonite K10 clay catalysed Friedel-Crafts aralkylation of compound **2** with a number of aromatic hydrocarbons furnished functionalised linear Aryl-Alkyl-Aryl systems in good yield. A comparative study of this reaction was carried out with mont-K10 and Fe^{3+}-Mont-K10.

Solid acid catalysed organic reactions constitute an important area in preparative and industrial organic chemistry.[1] Among the various organic reactions, the Friedel-Crafts aralkylation is important due to its wide application in the preparation of large number of industrial organic chemicals.[2] There are number of procedures known in the literature[3] for the Friedel-Crafts reactions. However, all these are acid catalysed, and the catalyst have to be used in high concentrations. The catalysts are non-recoverable, and entail problems of corrosion, workup and effluent pollution. Recently a wide range of organic reactions have been catalysed by clays which act as solid Lewis or Bronsted acids.[4]

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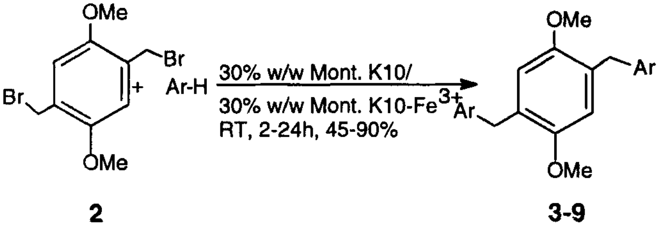
Montmorillonite clay is an ecofriendly, inexpensive, stable catalyst and has several advantages over conventional acids. It is strongly but non-corrosive and the reaction condition are generally mild, the workup is easy and the products are obtained in high yields with selectivity.

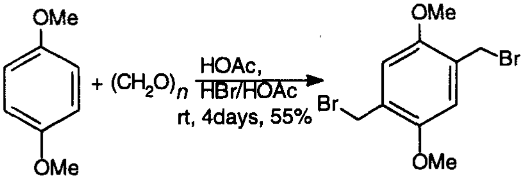
In continuation of our studies[5] in clay catalysed organic reactions, we have explored the clay catalysed Friedel-Crafts aralkylation reaction of compound **2** and the results are presented in this paper. The schematic representation of the present study is shown in scheme 1.



2 **3-9**

Scheme 1

Stirring the compound **2** with excess of aromatic hydrocarbon in presence of 30% w/w of montmorillonite-K10 at room temperature without any solvent (in case of solid hydrocarbons dichloromethane was used as solvent) afforded a colorless crystalline solid **3** (m.p : 100-102 °C purified by column chromatography) in 85% yield. The starting compound **2** (M.p: 201-203 °C) was prepared according to the literature procedure.[6] (Scheme 2)



1 **2**

Scheme 2

Compound **3** showed IR absorption bands at ν_{max} 3060, 1605, 1590 (aromatic), 1245, 1030 cm-^{1}. The ^{1}H NMR (300 MHz) showed peaks at δ 7.2 and 6.7 two multiplets for aromatic protons; at δ 3.9, a singlet for methylene

Table 1. Friedel-Crafts aralkylation of 2 with arens promoted by Mont- K10 and Mont K 10-Fe^{3+}. [a, b, c]

Entry	Arene	Reaction Time(h)		Product(s)[d]	M.p (°C)	Yield[e] (%)	
		K10	Fe^{3+}-K10			K10	Fe^{3+}-K10
1	Benzene	4	2	**3**	100-102	85	90
2	Toluene	5.5	3	**4**	112	74	82
3	o-Xylene	8	4.5	**5**	119	62	69
4	p-Xylene	7.5	4	**6**	132	60	70
5	Biphenyl[f]	18	24	**7**	171	45	52
6	Naphthalene[f]	16.5	22	**8**	182	48	54
7	Anthracene[f]	20	24	**9**	191	46	51

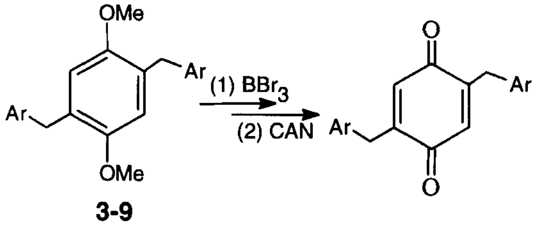
[a] The clay was dried at 85 °C for 2h before each reaction. [b] 30%(w/w)Montmorillonite -K10 clay was used for each case. [c] For conditions see typical experimental procedure [d] The homogeniety of the compounds was established by chromatographic techniques [e] Isolated after column purification. [f] Reaction was carried out in dichloromethane

protons and at δ 3.6, a singlet for OCH$_3$ protons. Since compound **3** is symmetric in nature, it showed the following ^{13}C NMR peaks at δ 151.3, 141.0, 128.2, 125.7, 113.6, 56.1, 35.8, 29.4.

The GCMS showed a molecular ion peak at *m/z* 318(M$^+$). The compound was also characterized by DEPT-135 spectrum where it showed a characteristic CH$_2$- negative peak at δ 56.1. The results are summarised in table 1. All the compounds reported herein gave satisfactory spectral and mass spectral data.

We have observed that when the reaction temperature was raised to 50 °C, the reaction time was considerably reduced albeit with 5-10% reduction in product yield. When these reactions were repeated with Fe^{3+}- Mont-K10 clay[7] (an ion-exchanged clay) the yields were found increased with reduced reaction time considerably (See table 1).

The recovered clays can be recycled three times after activating at 100 °C for 3h. The compounds reported herein can be used as starting material for the preparation of synthetically useful various substituted symmetrical *p*-quinones by treating with BBr_3 followed by CAN oxidation (Scheme 3). Further studies in this direction are underway.



Scheme 3

EXPERIMENTAL SECTION

General Considerations:

All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Nicolet Impact 400D spectrophotometer. All NMR studies are carried out on BRUKER DPX 300 MHz FT NMR spectrophotometer as indicated. Chemical shifts are reported in ppm (δ) with TMS as standard and coupling constants are expressed in Hertz. High resolution mass spectra were recorded on a Varian MAT-CH7 instrument at 70 eV. Thin layer chromatograms (TLC) were developed on glass plates coated with silica gel-G (ACME) of 0.25 mm thickness and visualized with iodine. Column chromatography was carried out with silica gel (ACME, 100-200 mesh) using hexane-ethyl acetate mixture as eluent. The organic extracts of crude products were dried over anhydrous $MgSO_4$. Solvents were reagent grade and were purified according to the literature procedure.[8]

Typical Experimental Procedure:

A mixture of **2** (5 mmol), aromatic hydrocarbons (15 mmol) and Montmorillonite K-10 / Mont-K10- Fe^{3+} (30% w/w of **2**) was stirred at room temperature in the case of solid reactants, 15 mL of dichloromethane was used as solvent) and the reaction was monitored by TLC. After the completion of the reaction, the mixture was treated with methylene chloride (20 mL). Montmorillonite K-10 was recovered by filtration and washed with methylene chloride (2 x 5 mL). The solvent was removed under reduced pressure to afford the crude material. The crude mixture was chromatographed over silica gel column using petroleum ether and a mixture of ethyl acetate with petroleum ether (1:9). The fractions containing the required product were concentrated to afford the expected product. The product was further purified by crystallisation from ethanol for further spectral analysis.

Spectral data for some selected compounds:

Compound 3[9]

M.pt. : 100-102 °C ; IR (CCl_4) ν_{max}: 3060, 1605, 1590, 1245, 1030 cm-^{1}.; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 7.2 (m, 10H, Ar-H), 6.7 (m, 2H, Ar-H), 3.9 (s, 4H, CH_2), 3.6 (s, 6H, OCH_3).; ^{13}C NMR (CDC13/TMS, 75.4 MHz): δ 151.3, 141.0, 128.2, 125.7, 113.6, 56.1, 35.8, 29.4. HRMS: Calcd for $C_{22}H_{22}O_2$: 318,4018; Found: 318.4012.

Compound 4:

M.pt. : 110-112 °C ; IR (CCl_4) ν_{max}: 3060, 1605, 1590, 1245, 1030 cm^{-1}.; ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 7.2 (m, 8H, Ar-H), 6.8 (m, 2H, Ar-H), 3.9 (s, 4H, CH_2), 3.6 (s, 6H, OCH_3) 2.1 (s, 6H, CH_3).; ^{13}C NMR ($CDCl_3$/TMS, 75.4 MHz) : δ 150.2, 130.0, 129.5, 128.9, 125.6, 116.8, 113.6, 111.4, 56.0, 38.9, 33.0, 20.9. ; HRMS: Calcd for $C_{24}H_{26}O_2$: 346.4620; Found: 346.4585.

Compound 6 :

M.pt. : 132 °C ; IR (CCl_4) ν_{max}: 3064, 1609, 1590, 1244, 1032 cm^{-1} . ^{1}H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 7.2-7.0 (m, 8H, Ar-H), 6.9 (m, 2H, Ar-H), 3.8 (s, 4H, CH_2), 3.6 (s, 6H, OCH_3) 2.1 (s, 6H, CH_3), 1.9 (s, 6H, CH_3); ^{13}C NMR

($CDCl_3$/TMS, 75.4 MHz): δ 150.8, 138.0, 133.0, 128.5, 125.5, 124.8, 122.1, 113.2, 55.8, 36.0, 29.6, 28.7, 18.6.; HRMS: Calcd for $C_{26}H_{30}O_2$: 374.5154; Found: 374.5131.

Compound 8:

M.pt. : 181-182 °C ; IR (CCl_4) ν_{max}: 3060, 1605, 1590, 1245, 1030 cm^{-1}.; ^1H NMR ($CDCl_3$/TMS, 300.1 MHz): δ 7.5-6.9 (m, 14H, Ar-H), 6.8 (m, 2H, Ar-H), 4.0 (s, 4H, CH_2), 3.7 (s, 6H, OCH_3).; ^{13}C NMR ($CDCl_3$/TMS, 75.4 MHz): δ 151.3, 141.0, 129.0,, 128.2, 127.5, 126.3, 125.7, 124.2, 113.6, 56.1, 35.8, 29.4.; HRMS: Calcd for $C_{30}H_{26}O_2$: 418.3462; Found: 418.3440.

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