RESEARCH LETTER

Hydroarylation of arenes with styrenes using Montmorillonite K-10 as an efficient, selective, and recyclable catalyst

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Hydroarylation of styrene and its derivatives with arenes and heteroarenes was studied using Montmorillonite K-10 as an efficient, environmentally benign, economical, greener, and recyclable catalyst. The reaction gives 1,1-diarylalkanes with a very high selectivity and excellent yields in short time with greater substrate compatibility.

Keywords: Alkene; heterogeneous catalysis; hydroarylation; Markovnikov adduct; styrene

1. Introduction

Catalytic functionalization of arenes and heteroarenes has gained considerable interest in recent years due to its applications in the pharmaceutical, (1) agrochemical, (2) fine, and bulk chemical industry (3). It is one of the important methodologies for C–C bond formation in organic synthesis (4–6). Traditionally, acylation, alkylation, nitration, and halogenations of arenes were carried out by Friedel–Crafts reactions (7–9) for such transformations. However, these methods have several limitations like the use of stoichiometric amount of Lewis acids, drastic reaction conditions (i.e. high temperature, longer reaction time etc.), lower selectivity, over alkylation products and large amount of salt formation. Formation of new C–C bond in the aromatic ring requires multiple steps like protection, deprotection or incorporation of activating groups. Therefore, there is a need to develop an efficient, environmentally benign, and recyclable catalytic protocol for hydroarylation of arenes. Recently, several organometallic catalysts were found to be useful as an efficient tool for the environmentally benign C–H functionalization like Friedel–Crafts hydroarylation of the arenes with electron rich aromatic and heteroaromatic compounds (10). The products of these reactions contain diarylalkanes which have great importance as they are a part of various valuable biological active compounds and pharmaceutics such as papaverine, beclobrate, phenprocoumene, dimetindene, haplopparin, nafenopin, and avrainvilleol trimethoprim (Figure 1). Various catalysts like FeCl₃, CoBr₂, Ir(III) complex, bimetallic nanoporous FeAl-KIT-5 catalyst, Bi(OTf)₃, BiBr₃, BiCl₃, I₂, and Sm(OTf)₃ are reported for this transformation (4, 11–19).

Usually, hydroarylation of arenes is catalyzed by homogeneous non-recyclable catalysts. Hence, the review of literature suggests that there are still challenges in developing a greener and metal free protocol for the hydroarylation of arenes. In contrast, Bronsted solid acids (20, 21) catalyzed methods have gained important attention over the decades and now they are widely preferred for various organic transformations. Among the several solid acid catalysts Montmorillonite K-10 is a one of the inexpensive, greener, and commercially available catalyst (22–26).

Herein, we introduced new application of Montmorillonite K-10 as a catalyst for the synthesis of 1,1-diarylalkane, via the reaction of styrene with arene. The catalyst was found to be highly efficient, selective, environmentally benign, scalable, and recyclable (Scheme 1).

2. Results and discussion

2.1. Optimization of the reaction parameters

Initially, the hydroarylation of anisole with styrene was chosen as a model reaction. Various reaction parameters such as catalyst screening, catalyst loading, solvent effect, molar ratio of substrate, reaction time, and temperature were investigated for this transformation. The results obtained were summarized in (Table 1). Various Bronsted acid and solid
acid catalysts such as \( p \)-Toluene sulphanic acid \((p\text{-TSA})\), Cu(OTf)\(_2\), Montmorillonite K-10, [NMPH\(^+\)]\(_2\)SO\(_4\), ZnCl\(_2\), ZrOCl\(_2\), and tungstophosphoric acid (TPA) were screened (Table 1 entries 1–7), wherein Montmorillonite K-10 was found to be the best catalyst providing 75% yield of the desired \( para \)-alkylated product (Table 1, entry 3) under the screening conditions. It was noted that when the reaction was carried out in the absence of catalyst, there was no product formation thus emphasizing that the Montmorillonite K-10 was solely responsible to catalyze the reaction with higher yield (Table 1, entry 8). To obtain the optimum amount of catalyst, the catalyst amount was varied in the range of 60–100 mg (Table 1, entries 9–11). The optimum results were obtained with 80 mg of Montmorillonite K-10 as a catalyst; further increase in catalyst amount had no significant effect on the yield of desired \( para \)-alkylated product (Table 1, entry 11). We observe that reaction was more favorable under solvent free condition rather than conventional organic solvents because arene itself can act as a very good solvent (Table 1, entries 12–14). The other reaction parameters like reaction temperature, substrate ratio for styrene:arene and reaction time were also studied (see Table 1, entries 15–27). On the basis of these, the optimized reaction conditions for hydroarylation of arenes with styrenes are: styrene:arene (1:10), catalyst Montmorillonite K-10 (80 mg), solvent (neat), at 80°C, for 0.5 h.

2.2. Characterization of catalyst

2.2.1 TGA analysis
The thermogravimetric analysis of the Montmorillonite K-10 was carried out to provide information on the degradation pattern when decomposed under nitrogen. The catalyst was found to be stable up to 101.6°C with a weight loss of only 8.9% which might be due to the water content loss. After that it undergoes very slow decomposition up to 550°C. Hence, the decomposition temperature of the catalyst was determined to be more than 550°C. A total weight loss of 12.5% was observed at 550°C. Thus, Thermogravimetric analysis (TGA) of the Montmorillonite K-10 catalyst shows that the catalyst is thermally stable at the reaction temperature (Figure 2).

2.2.2 TPD analysis of Montmorillonite K-10 catalyst
The TPD analysis of the catalyst Montmorillonite K-10 was carried out on model AutoChem II 2920 V3.03 at a flow rate of 40.05 mL STP/min. The acid-base properties are regarded as being the main factor that can influence significantly the clay behavior, NH\(_3\)-TPD measurements were performed on Montmorillonite K-10. The total number of acidic sites expressed in terms of millimoles of ammonia desorbed per gram of dry Montmorillonite K-10 on increasing temperature. The range of desorption temperature is 74–450°C and NH\(_3\)-TPD indicates higher acidity at 74°C, that is 9.23 mL/g (Figure 3).
2.2.3 Surface area analysis of Montmorillonite K-10 catalyst

Surface area and pore volume of the Montmorillonite K-10 was measured using surface area analyzer model SMART SORB 93 (N₂ adsorption-BET Dynamic method). The surface area of Montmorillonite K-10 was 215 m²/gm. The total pore volume of Montmorillonite K-10 was (At N₂ P/P₀ = 95%) 0.2797 cc/gm. From this total pore volume, we calculated the average pore diameter of Montmorillonite K-10 is 52.522 Å. For regeneration conditions the catalyst was kept in furnace at 100°C for 1 h and then used further for BET surface area analysis.
2.3. Substrate compatibility
We explored the scope of the Montmorillonite K-10 catalyzed hydroarylation of various arene with styrene and its derivatives under optimized reaction conditions (Table 2). In general, 1,1-diarylalkanes were prepared from the reaction of arene with good yield in short reaction time (0.5–6 h). In all the cases para-substituted products was obtained as the major product but for the phenol and its derivatives gave ortho-substituted products as a major product. For generalization of Montmorillonite K-10 catalyzed hydroarylation under optimized condition, we decided to explore protocol for differently substituted arenes with styrene (Table 2, entries 1–11) which gives moderate to high yield. We have also studied electron rich arenes like anisole for hydroarylation which gave 98% yield of para-arylated 1,1 diarylalkane (Table 2, entry 1), whereas phenol and its derivatives gave ortho-arylated product with very good yield as well as selectivity (Table 2, entries 2–7). Less reactive...
Table 2. Hydroarylation of styrene and its derivatives with arenas.

![Diagram showing hydroarylation of styrene with arenes.]

| No | Arenes | Product | Time (h) | Conversion (%) \(^{a}\) | Yield (%) \(^{a}\) | Selectivity (%) \(^{a}\) |
|----|--------|---------|----------|----------------|---------------|------------------|
| 1  | ![Structure](image1) | ![Structure](image2) | 0.5      | 100            | 98            | 86:14            |
| 2  | ![Structure](image3) | ![Structure](image4) | 6        | 97             | 80            | 70:30            |
| 3  | ![Structure](image5) | ![Structure](image6) | 6        | 100            | 98            | 100              |
| 4  | ![Structure](image7) | ![Structure](image8) | 6        | 99             | 95            | 69:31            |
| 5  | ![Structure](image9) | ![Structure](image10) | 6        | 95             | 95            | 79:21            |
| 6  | ![Structure](image11) | ![Structure](image12) | 6        | 98             | 35            | 100              |
| 7  | ![Structure](image13) | ![Structure](image14) | 6        | 90             | 30            | 100              |
| 8  | ![Structure](image15) | ![Structure](image16) | 6        | 100            | 40            | 70:30            |
| 9  | ![Structure](image17) | ![Structure](image18) | 6        | 92             | 70            | 99:1             |
| 10 | ![Structure](image19) | ![Structure](image20) | 6        | 100            | 95            | 90:10            |
| 11 | ![Structure](image21) | ![Structure](image22) | 6        | 95             | 85            | 100              |

**Reaction of styrene with different arenes**

**Reaction of α-methyl styrene with different arenes**

| No | Arenes | Product | Time (h) | Conversion (%) \(^{a}\) | Yield (%) \(^{a}\) | Selectivity (%) \(^{a}\) |
|----|--------|---------|----------|----------------|---------------|------------------|
| 12 | ![Structure](image23) | ![Structure](image24) | 6        | 100            | 95            | 87:13            |
| 13 | ![Structure](image25) | ![Structure](image26) | 6        | 100            | 92            | 65:5:30          |
substrates like toluene, ortho-, meta-, and para-xylenes were also reacted very smoothly and cleanly giving moderate to high yield of the desired products using Montmorillonite K-10 catalyst (Table 2, entries 8–11). α-Methyl styrene under acidic condition reacted with activated arene and gives the selectively para-arylated product in 90–95% yield (Table 2, entry 12–16). The reaction of sterically hindered 4-tert-butyl styrene with anisole provided a mixture of para- and ortho-alkylated anisole in 90% and 10%, respectively (Table 2, entry 17). Moreover, it was observed that the sterically hindered 4-tert-butyl styrene smoothly undergoes arylation with different arene derivatives providing 80–100% yield of expected products. The proposed method of hydroarylation of styrene was proved to be efficient, affording good yields of 1,1-diarylalkane with arenes. Synthesized 1,1-diarylalkanes were characterized by 1H NMR, 13C NMR, IR, and mass spectroscopy (see Supporting information).

### 2.4. Recyclability of the catalyst

Montmorillonite K-10 based protocol is considered to be greener, as the catalyst can be separated easily from the reaction mixture by simple filtration and recycled further. Hence, recycling experiments were conducted. It was observed that the catalyst can be recycled for four consecutive cycles with same activity and selectivity. No significant decrease in yield during the four recycles was observed. The yield declined up to 88% for the fifth cycle (Table 3).

| No | Arenes | Product | Time (h) | Conversion (%)<sup>a</sup> | Yield (%)<sup>a</sup> | Selectivity (%)<sup>a</sup> |
|----|--------|--------|----------|---------------------------|----------------------|---------------------------|
| 14 | OH     | OH     | 6        | 100                       | 90                   | 100                       |
| 15 |       |       | 6        | 100                       | 94                   | 90:10                     |
| 16 |       |       | 6        | 100                       | 90                   | 100                       |
| 17 | O      | O      | 6        | 100                       | 95                   | 90:10                     |
| 18 |       |       | 6        | 100                       | 95                   | 100                       |
| 19 | OH     | OH     | 6        | 100                       | 80                   | 100                       |
| 20 | O      | O      | 6        | 100                       | 85                   | 100                       |
| 21 |       |       | 6        | 20                        | 10                   | 100                       |

<sup>a</sup> Reaction and conditions: styrene (1 mmol), arene (10 mmol), Montmorillonite K-10 (80 mg), reacted at 80°C, <sup>GC</sup> yield, and <sup>b</sup>selectivity (ortho:meta:para).
The products were characterized using 1H NMR, 13C NMR spectra (Varian mercury 300 NMR spectrometer) and IR (Perkin-Elmer FT-IR) spectroscopic techniques. Surface morphology and elemental content in Montmorillonite K-10 was studied by SEM-EDAX analysis; TPA-TPD for Bronsted acidity study; BET dynamic method for surface area, total pore volume and average pore diameter analysis. The progress of reaction was monitored using GC analysis (Perkin-Elmer clarus 400) (BP-10 GC column, 30 m × 0.32 mm ID, film thickness 0.25 mm). Products were confirmed by GC-MS (Shimadzu GC-MS QP 2010). All products are known in the literature.

4.2. Typical experimental procedure for the hydroarylation of alkenes with arenes

In a 10 mL of sealed tube with a spin bar, alkene (1 mmol), arene (10 mmol), and Montmorillonite K-10 catalyst (80 mg) were taken and sealed properly. The reaction mixture was heated at 80°C with stirring for desired time and was cooled to room temperature on completion of reaction. Alkene conversion as well as product formation was monitored by gas chromatography. After completion of reaction mixture was diluted with ethyl acetate (5 mL), filtered off and washed with ethyl acetate (3 × 5 mL). The organic solution was analyzed with GC. The residue obtained was purified with column chromatography (silica gel, 60–20 mesh; PE-EtOAc, 95:05) to afford the desired hydroarylated products. The structure of obtained product confirmed by GC-MS, 1H NMR, 13C NMR, and IR spectroscopic techniques (see Supporting information). The purity of compounds was determined by GC-MS analysis.

4.3. Typical procedure of recycling Montmorillonite K-10 catalyst for hydroarylation of anisole with styrene

After completion of reaction, the reaction mixture was cooled to room temperature reaction mixture was diluted with ethyl acetate (5 mL). The catalyst was filtered off and washed with ethyl acetate (3 × 5 mL). Then, separated catalyst was dried at 80–85°C in oven for 1 h and used further for the catalyst recyclability experiment. It was observed that the recovered catalyst could be reused for the five consecutive cycles for the hydroarylation of anisole with styrene through slight decrease in yield of desired product.

4.4. Characterization of selected compound 2-[1-(4-tert-Butyl-phenyl)-ethyl]-4-methoxy-phenol (Table 2, entry 20)

4.4.1. Colorless liquid

1H NMR (300 MHz, CDCl3): δ = 1.25 (s, 3H), 1.57 (d, J = 7.33 Hz, 3H), 3.74 (s, 3H), 4.27 (q, J = 7.08 Hz, 1H), 4.35 (s, 1H), 6.65 (d, J = 2.57 Hz, 1H), 6.67 (s, 1H), 6.81 (d, J = 2.57 Hz, 1H), 7.15 (d, J = 8.43 Hz, 2H), 7.27 (d, J = 8.43 Hz, 2H); 13C NMR (75.43 MHz, CDCl3): δ = 21 (CH3), 29.1 (CH), 31.3 (3CH3), 38.2 (C), 55.6 (OCH3), 111.4 (CH), 114.3 (CH), 116.5 (CH), 125.5 (CH2), 127.1 (CH2), 133.7 (C), 141.9 (C), 147.4 (C), 149.1 (C), 153.6 (C); IR (KBr) ν = 3411, 2963, 1506, 1462, 1429, 1363, 1269, 1203, 1034, 836, 801, 713, 578 cm⁻¹; MS (EI, 70 ev): m/z (%) = 284 (57), 269 (48), 228 (16), 213 (15), 198 (4), 165 (4), 150 (100), 135 (21), 120 (23), 91 (12), 77 (7), 57 (21).

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Table 2- entry no 12- 1H NMR (CDCl3, 400MHz):
1-methoxy-4-(2-phenylpropan-2-yl)benzene
38.47, 115.75, 126.22, 127.48, 127.72, 128.44, 128.53, 129.78, 131.81, 145.51 and 150.99.

6.58 (d, 1H, J = 3 Hz); 7.24-7.26 (m, 4H, J = 3 Hz, 6 Hz).
13C NMR (CDCl3, 100.6MHz): δ 30.82, 42.18, 55.02, 113.18, 125.46, 150.61, 150.99.

4-methyl-2-(2-phenylpropan-2-yl)benzene
Table 2- entry no 14- 1H NMR (CDCl3, 400MHz): δ 1.67 (s, 3H); 2.35 (s, 3H); 3.58 (s, 1H); 7.32-7.33 (m, 4H), 7.33-7.34 (m, 4H). 13C NMR (CDCl3, 100.6MHz): δ 20.91, 30.16, 41.56, 117.55, 125.94, 126.84, 126.95, 128.41, 129.09, 129.54, 135.03, 148.46 and 151.52.
Table 2- entry no 2- $^1$H NMR of 2-(1-phenylethyl)phenol

![Chemical structure and NMR spectrum]

Table 2- entry no 2- $^{13}$C NMR of 2-(1-phenylethyl)phenol

![Chemical structure and NMR spectrum]
Table 2- entry no 3- $^1$H NMR of 4-methyl-2-(1-phenylethyl)phenol

![1H NMR spectrum of 4-methyl-2-(1-phenylethyl)phenol](image1)

Table 2- entry no 3- $^{13}$C NMR of 4-methyl-2-(1-phenylethyl)phenol

![13C NMR spectrum of 4-methyl-2-(1-phenylethyl)phenol](image2)
Table 2- entry no 12- $^1$H NMR of 1-methoxy-4-(2-phenylpropan-2-yl)benzene

![NMR spectrum of 1-methoxy-4-(2-phenylpropan-2-yl)benzene](image)

Table 2- entry no 12- $^{13}$C NMR of 1-methoxy-4-(2-phenylpropan-2-yl)benzene

![NMR spectrum of 1-methoxy-4-(2-phenylpropan-2-yl)benzene](image)
Table 2- entry no 14. $^1$H NMR of 4-methyl-2-(2-phenylpropan-2-yl)phenol

Table 2- entry no 14. $^{13}$C NMR of 4-methyl-2-(2-phenylpropan-2-yl)phenol