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Catalysts and Process for the Production of Benzyl Toluenes

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Abstract:

A method for the synthesis of benzyl toluenes from toluene and using molecular bromine as catalytic operator is reported here. The process can be carried out in one of two ways: the first method involves the simultaneous bromination/alkylation of toluene, followed by recycling of the liberated HBr to an oxidation reactor to form molecular bromine; the second method involves the formation of benzyl bromide in a separate step with in situ bromine recycling, followed by alkylation of toluene. HBr liberated during the alkylation step is recovered and recycled in the bromination reactor. Solid catalysts that maximize side-chain bromination over ring bromination, whilst at the same time catalysing the Friedel−Crafts condensation of toluene with benzyl bromide, are key to the success of the process.

Introduction

Benzyl toluene and isomeric mixtures thereof are compounds useful as dielectric liquids for such components as transformers, capacitors, and cables. The synthesis of benzyl toluene and related compounds is normally carried out by the Friedel−Crafts condensation of a benzylic halide with an aromatic compound in the presence of a Friedel−Crafts catalyst.[1] After condensation, the catalyst is destroyed by, for example, adding a dilute aqueous solution of hydrochloric acid, followed by a washing of the organic phase.

The said compounds may alternatively be synthesised by adding a catalytically effective amount of a metal halide such as ferric chloride to a mixture of aromatic halide and aromatic compound.[2] This process has been claimed to be simpler compared with the above process in that no downstream destruction of the catalyst by neutralization or washing is required.

In yet another method,[3] a mixture of benzyl and methylbenzyl toluenes is produced by reactions involving alkylation and transalkylation at high temperatures, which then requires a complex separation and purification step to obtain the desired product.

In all of the above-mentioned methods, a significant disadvantage is that the organic halide has to be synthesized in a separate process step. Although the method by Commandeur et al.[2] allows for the direct addition of a Friedel−Crafts catalyst to the halogenating reaction mixture without separation of the organic halide, relatively low yields of the desired benzyl toluenes (<85%) are formed.

Salmon and co-workers[4] have reported a one-pot preparation of the desired product using bromine and toluene in the presence of a commercial bentonitic earth as catalyst with an 85% product yield. Catalysis of organic reactions by inorganic solids is an important dimension of preparative organic chemistry.[5] Specifically, smectite clays, doped with transition metal ions, are known to catalyse alkylation reactions of aromatic substrates. Clays containing zinc (II)[6,7] and iron (III)[8,9] have been reported to significantly enhance catalytic activities in these types of reactions. Laszlo and Mathy[10] have extensively studied Friedel−Crafts alkylations with halides, olefins, and alcohols using montmorillonite K10-supported transition metal ions and have reported good conversion rates and improved yields as compared with standard Lewis acid catalysts.

In this study, we report a versatile, highly efficient method for the condensation of toluene to produce benzyl toluene (the term “benzyl toluene” implies a mixture of the *o*-, *m*-, and/or *p*-isomers) in the presence of molecular bromine and a clay-supported transition metal catalyst. The ratio of meta-:ortho-:para-benzyl toluene obtained in this way was always approximately 8:40:52, respectively. The process offers several advantages, including bromination and alkylation reactions occurring simultaneously and in one pot, selective benzylic bromination with in situ bromine recycling, improved yield and selectivity to the desired product with insignificant amounts of side-product formation, and a convenient method for the recovery and subsequent air-oxidation of formed hydrobromic acid back to molecular bromine.

Results and Discussion

Scheme 1 illustrates the two possible routes investigated.

In Route A, the bromination of toluene and the Friedel−Crafts alkylation of toluene by benzyl bromide occur in one

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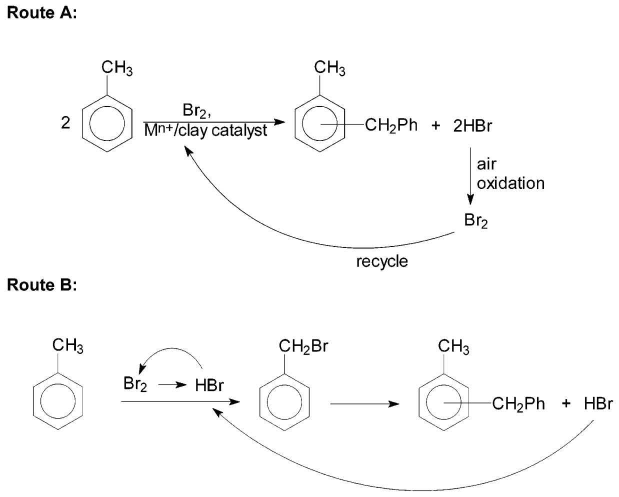
Table 1. **Bromination/alkylation of toluene with blank clays**

catalyst	drying temp (°C)	solvent	reaction temp (°C)	reaction time (h)	$C_6H_4BrCH_3$ (%)[a]	$C_6H_5CH_2Br$ (%)[a]	BzT[b] (%)[a]
bentonite[c]	-	-	110	4	2.7	9.1	68.0
montmorillonite K10[c]	-	-	110	4	5.5	36.2	41.2
bentonite	180	CCl_4	60	4	-	80.0	-
montmorillonite K10	180	CCl_4	60	4	9.6	76.4	-
bentonite	180	-	60	4	1.2	80.8	1.4
montmorillonite K10	180	-	60	4	3.6	81.6	7.3
bentonite	180	-	110	4	trace	64.5	23.0
montmorillonite K10	180	-	110	4	2.5	72.2	15.0
bentonite	120	-	110	4	3.0	0	80.6
montmorillonite K10	120	-	110	4	4.6	0	76.1
bentonite	90	-	110	4	1.9	0	83.6
montmorillonite K10	90	-	110	4	7.5	0	82.9

[a] Yields based on Br_2. [b] BzT = benzyl toluene [c] Used as received with no pretreatment.

Scheme 1. **Two possible routes for the production of benzyl toluene**



pot. HBr liberated is collected in glacial acetic acid and oxidised by air in the presence of sodium nitrate. Bromine formed in the oxidation reactor is displaced with excess air and recycled back to the bromination/alkylation reactor. In Route B, bromination of toluene occurs in a separate reaction vessel with in situ HBr recycling. HBr released during the alkylation step is recovered and recycled to the bromination reactor.

Simultaneous Bromination/Alkylation of Toluene (Route A). *Bromination/Alkylation of Toluene Using Pretreated Heat-Activated Clays.* Two smectite clays, bentonite and montmorillonite K10, were used as the basis of catalysts investigated in this study. To ensure uniform performance during the study, commercial samples of the two clays were initially pretreated by suspending the clay in an excess of deionised water for a brief period to allow any silicate materials to settle, followed by decantation and centrifugation to recover the clay. The clays so obtained were dried at various temperatures. These were then used in the bromination/alkylation reaction as blanks for comparative purposes. Results of the yields, based on Br_2, of ring-brominated side-products, intermediate benzyl bromide and final product benzyl toluene (determined by gas chromatography) are summarized in Table 1.

Table 2. **Alkylation of toluene using commercially obtained benzyl bromide**

drying temp (°C)	montmorillonite K10		bentonite	
	$C_6H_5CH_2Br$ conversion (%)[a]	yield BzT[b] (%)[c]	$C_6H_5CH_2Br$ conversion (%)[a]	yield BzT[b] (%)[c]
d	55.8	50.9	70.4	66.1
50	85.6	79.7	86.5	77.3
90	76.3	71.1	78.0	74.5
120	60.5	57.8	81.9	74.4
180	51.0	49.7	70.5	65.8
280	61.1	56.9	81.0	75.0

[a] Mol %. [b] BzT = benzyl toluene. [c] Mol %, based on benzyl bromide. [d] Clays used as received.

These results show that pretreatment and drying of the clays improves catalytic activity as compared to clays not treated in this fashion. However, it is apparent that high drying temperatures cause a decrease in catalyst activity, with an optimal drying temperature being in the range between 90 and 120 °C.

It is also of interest to compare the results described above to results obtained for the benzylation of toluene with commercially obtained benzyl bromide. These results are summarised in Table 2.

As with the simultaneous bromination/alkylation reaction, pretreatment of the clays improve catalytic activity. This is probably the result of the combined effect of increased surface area (by removing larger silicate particles) and improved intercalation of (nonpolar) toluene upon removal of excess surface and interlayer water upon drying. The observed decrease in catalytic activity at higher drying temperatures may possibly be the result of a decrease in the interlayer spacing upon heating[11] and/or a decrease in Brønsted acidity with increased water loss at higher drying temperatures.[12]

Bromination/Alkylation of Toluene Using Ion-Exchanged Metal-Modified Clays. The pretreated, activated clays were modified by the introduction of metal ions by means of ion exchange into the clay structure according to a known

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Table 3. **Bromination/alkylation of toluene using ion-exchanged clays**

catalyst	$C_6H_4BrCH_3$ (%)[a]	$C_6H_5CH_2Br$ (%)[a]	BzT[b] (%)[a]	total (%)[a]	selectivity[c] (%)[a]
K-montmorillonite K10	<1	80.1	14.3	94.4	>99
K-bentonite	<1	50.7	40.1	90.8	>99
Zr-montmorillonite K10	0	75.9	12.3	88.2	100
Zr-bentonite	9.6	50.2	14.3	74.1	87.0
Ba-montmorillonite K10	4.2	63.2	11.0	78.4	94.6
Ba-bentonite	3.61	0	73.5	77.1	95.3
Ce-montmorillonite K10	15.4	32.2	27.7	75.3	79.7
Ce-bentonite	38.4	0	40.4	78.8	48.7
Ti-montmorillonite K10	0.64	2.25	78.2	81.1	99.2
Ti-bentonite	3.14	0	75.3	78.4	96.0
Cu-montmorillonite K10	1.37	0	79.7	81.1	98.3
Cu-bentonite	4.01	0	78.6	82.6	95.1
Co-montmorillonite K10	11.7	0	70.4	82.1	85.7
Co-bentonite	20.1	0	64.2	84.3	76.2
Zn-montmorillonite K10	<1	0	86.4	86.4	>99
Zn-bentonite	9.46	0	73.6	83.1	88.6
Fe-montmorillonite K10	14.7	0	76.0	90.7	83.8
Fe-bentonite	35.7	0	45.7	81.4	56.1

[a] Percentage yields and selectivities based on Br_2. [b] BzT = benzyl toluene. [c] Selectivity = [(%$C_6H_5CH_2Br$ + % BzT)/% total products] × 100.

procedure.[10] Metal ions that were investigated are listed in Table 3. Ion exchange was achieved by contacting the pretreated clay with a 1 M aqueous solution of the metal chloride for 24 h with stirring. After this period followed by filtering and washing with deionised water, the catalyst was oven-dried, powdered, and used as such in the bromination/alkylation step. Results obtained are summarised in Table 3.

The first significant observation from these results is that ion-exchanged clays are much more effective than those that have not been subjected to ion exchange. In general, bentonite ion-exchanged catalysts were less selective than the corresponding K10 ion-exchanged catalysts, with the best selectivity being displayed by the K-K10, K-bentonite, Zr-K10 and Zn-K10 catalysts. It is, however, quite noticeable from the results shown that only the later transition metals (Cu, Co, Zn, and Fe) result in catalysts that show a significant improvement in Friedel−Crafts activity. In comparative experiments using commercial benzyl bromide, all the transition metals, with the exception of titanium, gave yields of benzyl toluenes between 95 and 100% after a reaction period of 20 min. Generally speaking, a high activity towards Friedel−Crafts alkylation also leads to a higher activity for ring bromination as can be seen from the entries for cerium, iron, cobalt and zinc.

Effect of Pre-ion Exchange Drying Temperature on Catalyst Selectivity. To demonstrate the importance of temperature treatment of the clay before ion exchange and activation after ion exchange, several catalysts were prepared by differing the heat treatments at different stages of catalyst preparation. In one case, pretreatment of the catalyst support was carried out as described previously, except that the clay was only air-dried at room temperature prior to ion exchange. After ion exchange, the catalyst was activated at different temperatures. In the second case, the blank clay was dried before ion exchange at different temperatures followed by drying at 120 °C after ion exchange. Catalysts so prepared were designated according to the method and conditions used during preparation. For example, if the clay was pretreated at 120 °C followed by ion exchange with Zn and subsequent activation at 180 °C, this is designated K10-120-Zn-180. The results obtained for the simultaneous bromination/alkylation of toluene using these catalysts are summarised in Table 4.

Table 4. **Effect of pre-ion exchange drying temperature on catalyst selectivity**

catalyst	yield (mol %) $C_6H_4BrCH_3$ (%)[a]	yield (mol %) BzT[b] (%)[a]	total (%)[a]	selectivity[c] (%)[a]
K10-Zn-120	56.8	28.4	85.2	33.3
K10-120-Zn-120	4.45	79.1	83.6	94.6
K10-180-Zn-120	<1	86.4	86.4	100
K10-Cu-120	24.2	58.0	82.2	70.6
K10-120-Cu-120	5.7	79.6	85.3	93.3
K10-180-Cu-120	1.4	79.7	81.1	98.3
Bent-Zn-120	82.8	14.7	97.5	15.1
Bent-120-Zn-120	31.9	45.8	77.7	58.9
Bent-180-Zn-120	9.5	73.6	83.1	88.6
Bent-Cu-120	22.3	61.5	83.8	73.4
Bent-120-Cu-120	19.2	58.1	77.3	75.2
Bent-180-Cu-120	4.0	78.6	82.6	95.1

[a] Percentage yields and selectivities based on Br_2. [b] BzT = benzyl toluene. [c] Selectivity = [(%$C_6H_5CH_2Br$ + % BzT)/% total products] × 100.

It is clear from these results that temperature activation of the support prior to ion exchange significantly decreases bromination of the aromatic ring and increases the selectivity towards benzylic bromination and subsequent benzyl toluene formation. Both Ca-montmorillonite and Na-montmorillonite have been shown to undergo a gradual loss in cation-exchange capacity on heating to 300 °C.[13] It is expected that the resultant decrease in metal loading on the clay supports affects radical (side-chain) bromination and Friedel−Crafts activity less than the nonradical ring bromination to result in a more selective catalyst.

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Table 5. **Effect of the rate of bromine addition**

addition time (min)	yield (mole %) $C_6H_4BrCH_3$ (%)[a]	$C_6H_5CH_2Br$ (%)[a]	BzT[b] (%)[a]	total (%)	selectivity (%)[a,c]
0[d]	9.7	5.8	81.0	96.5	89.9
0	18.7	0	76.1	94.8	80.2
10	27.0	0	55.0	82.0	67.1
30	38.6	0	45.8	84.4	54.3

[a] Percentage yields and selectivities based on Br_2. [b] BzT = benzyl toluene. [c] Selectivity = [(%$C_6H_5CH_2Br$ + % BzT)/% total products] × 100. [d] Undiluted, and added directly onto catalyst prior to toluene addition.

Bromination/Alkylation of Toluene with Various Rates of Bromine Addition. The importance of the rate and method of bromine addition on reaction selectivity was investigated. Several experiments were carried out in which molecular bromine was added to the reaction mixture, comprising substrate and catalyst, in one of four ways: (i) added in one batch, undiluted, (ii) added in one batch, diluted with inert solvent, (iii) continuous addition of diluted bromine over 10 min, and (iv) continuous addition of diluted bromine over 30 min. In each case, the catalyst used was K10-100-Zn-100, and the reaction was allowed to proceed for 15 min after complete bromine addition. All reactions were carried out at reflux temperature. Results obtained are summarized in Table 5.

The results suggest that a slower bromine addition rate favours ring bromination and hence results in a significant reduction in benzyl toluene formation. Interestingly, addition of bromine directly onto the catalyst such that the bromine could be adsorbed prior to contact of the catalyst with toluene led to higher selectivity toward benzylic bromination, as compared to addition of bromine to the catalyst/toluene mixture. In two further comparative experiments, toluene was first heated under reflux in the presence of the catalyst for one minute prior to the addition of diluted bromine as a single batch, and in the second experiment, diluted bromine was first heated under reflux in the presence of the catalyst before the addition of toluene to the mixture. The first reaction gave 82.0% benzyl toluene and 16.3% bromotoluene, while the second gave 96.5% benzyl toluene and 2.33% bromotoluene. It is of interest to note that the batch-wise addition of molecular bromine may be repeated several times without the need to separate the catalyst or reaction products or both.

Bromination/Alkylation of Toluene Using Metal-Coated Clays. The effect of modifying the clays by means of metal deposition was investigated. Here the metal used was Zn, and K10 was the support. The deposition was achieved by dissolving the metal salt in water, adding the resultant solution to the blank pretreated clay, evaporating off the excess solvent by rotary evaporation and finally oven-drying at 120 or 400 °C. After grinding finely, the modified clay was used for the simultaneous bromination/alkylation of toluene (Table 6).

The ion-exchanged catalyst K10-180-Zn-120 is much more selective towards benzylic bromination and benzyl toluene formation than the K10-180-Zn-120 catalyst prepared by the deposition technique. This is probably a reflection of the higher metal loadings achieved during deposition as compared to ion exchange and the resultant increase in Lewis acid sites on the metal-coated clays. As before, high temperature activation of metal-coated and ion-exchanged clays improves the selectivity towards benzylic bromination, without impacting too greatly on the Friedel−Crafts activity of the catalyst. Using an activation temperature of 400 °C for the ion-exchanged catalyst (K10-180-Zn-400) in this process afforded a yield of benzyl toluene of 97% with 99% selectivity.

Hydrobromic Acid Scrubbing and Oxidation. The gaseous hydrobromic acid that was released during the bromination and alkylation reactions was scrubbed from the reactor exit gas by bubbling through glacial acetic acid. The HBr so recovered (typically >95%) was oxidised to molecular bromine by air by adding a catalytic amount of sodium nitrate to the acetic acid/HBr mixture at a reaction temperature of 100 °C.[14] Molecular bromine formed during the oxidation was displaced from the oxidation reactor by the excess air fed to reactor. Molecular bromine recovery by cold trapping was typically in the order of 85−90% of the HBr present in the glacial acetic acid.

Consecutive Bromination and Alkylation of Toluene (Route B). An alternative approach to the preparation of the desired benzyl toluenes involves the initial bromination of toluene in a separate reactor followed by alkylation of toluene after isolation of benzyl bromide. This route involves two steps but has the advantage that HBr liberated during the bromination step can be recycled in situ. In addition, HBr liberated during the alkylation step can be recycled directly to the bromination reactor, thereby eliminating the need to handle molecular bromine at any stage of the process.

To evaluate the feasibility of such an approach, toluene was brominated with molecular bromine in glacial acetic acid using activated silica gel as catalyst in two ways. In the first, no recycling was attempted via oxidation using the sodium nitrate/air system, while in the second, oxidation of HBr liberated during the bromination step was attempted in situ. The results obtained for these two experiments are summarised in Table 7.

In the absence of $NaNO_3$, a high yield of the desired benzyl bromide was obtained with no detectable ring-brominated products being formed. In the presence of $NaNO_3$ and air, HBr released during the bromination step is effectively oxidised back to molecular bromine to give >95% bromine atom utilisation. Apart from benzyl bromide, a small amount of ring-brominated toluene was also obtained. These experiments have demonstrated that the reaction may be carried out effectively and efficiently in two separate process steps.

Experimental Section

Simultaneous Bromination/Alkylation of Toluene (Route A). *Bromination/Alkylation of Toluene Using Pretreated Heat-Activated Clays.* Montmorillonite K10 or bentonite (20 g) was suspended in deionized water (250 mL), stirred

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[14] McInnes, S. M.; Zeelie, B.; Hlohloza, S. N.; Hamilton, L. M. RSA Pat. 95/2274, Feb 28, 1996.

Table 6. **Method of catalyst preparation**

catalyst[a]	yield (mol %) $C_6H_4BrCH_3$ (%)[b]	$C_6H_5CH_2Br$ (%)[b]	BzT[c] (%)[b]	total (%)	selectivity (%)[b,d]
IX-K10-180-Zn-120	4.51	0	93.2	97.7	95.4
IX-K10-180-Zn-400	0.36	0.4	96.0	96.7	99.3
MC-K10-180-Zn-120	23.9	0	70.0	93.8	74.6
MC-K10-180-Zn-400	8.65	0	83.0	91.7	80.5

[a] IX = ion-exchanged; MC = metal-coated. [b] Percentage yields and selectivities based on Br_2. [c] BzT = benzyl toluene. [d] Selectivity = [(%$C_6H_5CH_2Br$ + % BzT)/% total products] × 100.

Table 7: **Bromination of toluene**

experiment	$C_6H_4BrCH_3$ (%)[a]	$C_6H_5CH_2Br$ (%)[a]
no $NaNO_3$	-	98.9
with $NaNO_3$	1.65	191.1

[a] Yield based on initial Br_2 charged.

rapidly for ca. 10 s, and left standing for ca. 1.5 min. The supernatant slurry was decanted and filtered by suction. The residue was further washed with deionized water four times before drying and activation at the required temperature. Toluene (15 mL), optionally diluted with CCl_4 (15 mL) and containing the activated clay (0.30 g), was treated with diluted molecular bromine (1 g in 15 mL of CCl_4) over a period of 45 min. The reaction was heated at the required temperature for 4 h, the catalyst filtered off, and the reaction mixture analysed by GC.

Alkylation of Toluene Using Commercially Obtained Benzyl Bromide. The pretreated clay (0.25 g), toluene (15.0 mL, 141 mmol) and benzyl bromide (0.64 g, 3.74 mmol) were weighed into a 100-mL round-bottomed flask, and the mixture was heated under reflux for 8 min. After this period, an aliquot (5 mL) was removed, quenched with a cold saturated NaCl solution (5 mL), and extracted with CCl_4 (3 × 5 mL). The organic layer was dried (Na_2SO_4), the drying agent filtered off, and the filtrate analyzed using GC.

Bromination/Alkylation of Toluene Using Ion-Exchanged Metal-Modified Clays. The clays were modified by metal ion exchange according to a known procedure.[10] To the metal ion solution (1 M, 50 mL), prepared by dissolving the metal chloride (0.1 mol) in deionized water (100 mL), was added the clay (4.0 g), pretreated as described above, while stirring rapidly with a Teflon-coated magnetic stirrer bar. Stirring was continued for 24 h after which the solid was filtered off, and washed with deionized water (10 × 15 mL) until no chloride could be detected in the wash water ($AgNO_3$ test). The catalyst was dried (120 °C, 8 h), finely ground, and stored in a desiccator until required. Toluene (15 mL) was treated with molecular bromine (1.0 g in 15 mL of CCl_4) over a period of 50 min in the presence of the catalyst (0.3 g). The reaction was heated under reflux and terminated after 4 h, and the reaction mixture was analysed by GC.

Bromination/Alkylation of Toluene with Various Rates of Bromine Addition. The catalyst K10-100-Zn-100 (0.225 g) was suspended in toluene (60 mL, 0.56 mol) in a 100-mL round-bottomed flask. Bromine (0.32 g; 2.0 mmol) in CCl_4 (10 mL) was added, at the various rates, to the stirred reaction mixture at 110 °C. An aliquot (5 mL) of the reaction mixture was sampled 15−20 min after bromine addition, quenched with sodium thiosulfate solution (0.1 M), extracted with CCl_4, and finally analysed by GC.

Bromination/Alkylation of Toluene Using Metal-Coated Rather than Ion-Exchanged Clays. The metal chloride (5 mmol) was dissolved in water (5.7 mL) and the pretreated and activated clay (5 g, activated at 180 °C) added to the solution. After thorough mixing, a thick paste was formed. The coated clay was then oven-dried at the required temperature (120 or 400 °C) and ground finely. Toluene (15 mL, 0.14 mol) and the required modified catalyst (0.1 g) were heated to 110 °C, and diluted molecular bromine (0.8 g, 5 mmol in 15 mL of CCl_4) was added in one batch. After 20 min, an aliquot (5 mL) was sampled, quenched with sodium thiosulfate (0.1 M), and extracted with CCl_4. The reaction mixture was analysed by GC.

Hydrobromic Acid Scrubbing and Oxidation. HBr scrubbing and oxidation were carried out according to a known procedure.[14]

Consecutive Bromination and Alkylation of Toluene (Route B). *Bromination of Toluene Using Molecular Bromine in the Absence of $NaNO_3$.* Toluene (28.19 g, 0.31 mol) and silica gel 60 (0.30 g) were weighed into a 100-mL round-bottomed flask. The mixture was heated under reflux while a solution of bromine (0.80 g, 5.0 mmol) in acetic acid (15 mL) was added dropwise. After the addition was complete, the reaction mixture was heated and stirred until complete discolouration had occurred, indicating a completed reaction. The mixture was cooled, the silica removed by filtration, and the filtrate analysed using GC.

Bromination of Toluene Using Molecular Bromine in the Presence of $NaNO_3$. The reaction was repeated as described above with the exception that $NaNO_3$ (0.52 g, 6.1 mmol) was added to the mixture in the round-bottomed flask prior to reflux and bromine addition.

Alkylation of Toluene with Benzyl Bromide. This was carried out according to the procedure described previously herein.

Conclusions

A simple, one-pot synthetic route to benzyl toluene, from toluene as feedstock, has been investigated using molecular bromine over modified inorganic clays. The two main reactions comprising the synthetic procedure, benzylic bromination of toluene and Friedel−Crafts benzylation of toluene, are both catalysed by these modified clays. The activity of montmorillonite K10 and bentonite for the Friedel−Crafts alkylation reaction was dramatically increased by modifying the clays with metal ions, either through the process of ion exchange or by surface coating. These catalysts were mild alkylation catalysts, affording few or no unwanted side reactions. The selectivity and yield achieved in the optimum process was 99% and 97%, respectively. The preparation of benzyl toluene was also successfully carried out in two process steps, with near-quantitative bromine atom utilisation being noted in the recycle stage of the process.

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