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Montmorillonite KSF-catalysed regioselective *trans*-*tert*-butylation of *tert*-butylphenols

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Abstract—*ortho*-Regioselective de-*tert*-butylation of poly-*tert*-butylphenols is performed by treatment with montmorillonite KSF as a cheap, green and reusable catalyst. The procedure can be utilised for converting an equimolecular mixture of 2,4-di-*tert*-butylphenol and phenol into the more precious 4-*tert*-butylphenol (77% yield, 93% selectivity). © 2001 Elsevier Science Ltd. All rights reserved.

The *tert*-butyl group is frequently utilised as a positional protective group for the selective preparation of functionalised aromatic compounds with particular interest into the phenol derivatives.[1] In fact, specific experimental conditions have been found for the selective introduction and removal of this protective and/or blocking group.[2] In general removal of a *tert*-butyl group from aromatic compounds requires the use of an excess of $AlCl_3$ or similar hard Lewis or protic acids.[3]

The use of stoichiometric reactions and traditional synthetic and purification procedures has been recognised by R. A. Sheldon as the reason for the production of impressively large amounts of waste in the manufacture of fine chemicals and pharmaceuticals.[4] Thus, cleaner catalytic technologies are requested with particular attention to the use of heterogeneous, easily available and reusable catalysts.

Our current interest in the exploitation of solid acids for fine chemicals preparation,[5] has led us to re-examine the *tert*-butyl transfer from *tert*-butylphenols promoted by KSF montmorillonite clay.[6] Kinetic studies on the microwave-activated catalytic de-*tert*-butylation of *tert*-butylphenols on KSF catalyst were recently reported.[7]

We decided to perform experiments without application of microwaves since this technique causes a reduction in the surface area of the solid catalyst and consequently lowers its efficiency and prevents its reusability.[8]

In a first series of experiments *ortho*-, *meta*- and *para*-*tert*-butylphenols **1a**, **1b** and **1c** (Fig. 1) (1 mmol, 0.15 g each) were separately heated in toluene (25 ml), utilised as solvent and acceptor for the detached *tert*-butyl group, at 110°C for 4 h in the presence of KSF clay (1.0 g).[9]

Products detected in the reaction mixtures were the unreacted starting *tert*-butylphenol **1**, the parent phenol **2** and *tert*-butyltoluenes.[10] Production of isomeric and poly-*tert*-butylphenols via an isomerisation–transalkylation reaction involving the starting *tert*-butylphenol **1**[11] was completely prevented due to the use of a large excess of toluene. Yield of phenol **2** produced versus time is depicted in Fig. 2. The conversion of com-

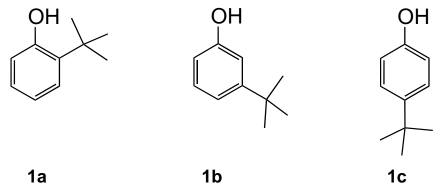

Figure 1. *tert*-Butylphenols utilised.

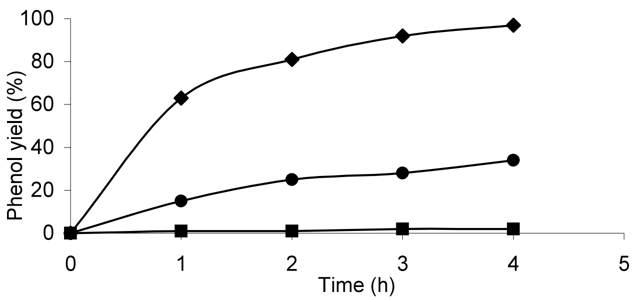

Figure 2. Phenol yield produced from *ortho*- (◆), *meta*- (■) and *para*-*tert*-butylphenol (●).

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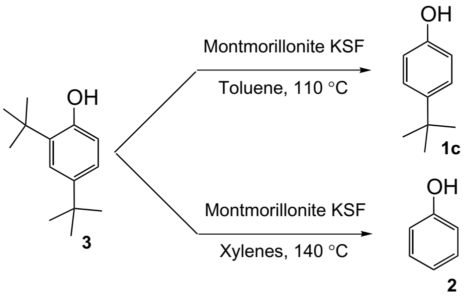
pounds **1** in phenol **2** follows the order **1a** (97%) >**1c** (38%)≫**1b** (traces) in agreement with results obtained in $AlCl_3$-promoted similar reactions;[1,2,12] the selectivity is always higher than 98%.

The more rapid increase of phenol production from **1a** compared with **1c** may be explained by the influence of the OH group, which favours the *ortho*-dealkylation more than the *para* by the 'proximity effect' as in the case of the preferential *ortho*-regioselective *tert*-butylation of phenol substrates promoted by an OH group.[13]

The reactivity of 2,4-di-*tert*-butylphenol **3** was successively examined with the aim of achieving selective mono- or bis-de-*tert*-butylation reaction (Scheme 1).

Compound **3** (2.5 mmol, 0.52 g) was heated in toluene (25 ml) at 110°C under stirring in the presence of KSF clay (1 g). Results of the conversion of **3** and yields of **1c** and **2** versus time are depicted in Fig. 3.

The de-*tert*-butylation is much faster at the *ortho* position in agreement with similar reactions performed under homogeneous catalysis. Consequently, compound **1c** could be produced in 75% yield and 96% selectivity after 14 h, whereas production of phenol **2** represents a side reaction occurring for a longer reaction time. Under harder conditions (namely 140°C in xylenes for 4 h and with 1 g of KSF clay per mmol of **3**) phenol **2** is quantitatively produced by complete bis-de-*tert*-butylation of **3**.



Scheme 1.

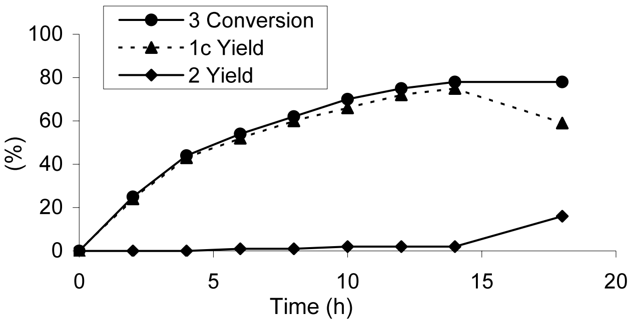


Figure 3. Influence of reaction time on the selectivity of the process.

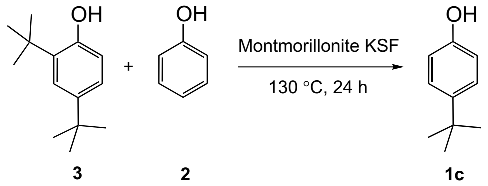
These results prompted us to investigate the regioselective *tert*-butyl transfer from the *ortho* position of **3** to the *para* position of **2** to give **1c**. This reaction shows considerable practical interest since the two low value compounds **3** and **2** can be simultaneously converted into the more precious compound **1c**. Compounds **3** (2 mmol, 0.41 g) and **2** (2 mmol, 0.19 g) were heated at 130°C for 24 h in the presence of KSF clay (1 g) in different solvents.

Results from Table 1 suggest that the selectivity towards the formation of **1c** was very high in all cases. Moreover, the catalytic efficiency is slightly influenced by the polarity parameter of the solvent provided that solvents with $E_T(30)$[14] <40 are utilised (entries 1–5). The low reactivity of the present system in highly polar solvents could be attributed to the preferential adsorption on the catalyst surface of solvent molecules with respect to the phenolic reagents. However, the best results were obtained by carrying out the reaction without a solvent, which represents more environmentally friendly conditions.

Finally, we faced the problem of catalyst recycling in the model reaction with *ortho*-*tert*-butylphenol **1a**. Montmorillonite KSF, recovered at the end of the reaction by Büchner filtration, washed with hot methanol and dried under vacuum at rt, was reused for at least two further cycles showing the following yields (selectivities): 96 (97), 94 (98).

In conclusion, treatment of *tert*-butylphenols with the cheap and easily available montmorillonite KSF results in the mild, safe and selective de-*tert*-butylation of mono and di-*tert*-butylphenols. Moreover, *para*-*tert*-butylphenol can be produced by selective *trans*-alkylation from 2,4-di-*tert*-butylphenol to phenol itself. Finally, the solid catalyst can be filtered off and reused showing similar high yield and selectivity.

Table 1. Solvent effect in transalkylation reaction involving 2,4-di-*tert*-butylphenol and phenol



Entry	Solvent	$E_T(30)$	**1c** Yield[a] [sel.[b]] (%)
1	Decaline	31.2	62 [94]
2	Chlorobenzene	36.8	66 [98]
3	Tetrachloroethylene	39.4	68 [98]
4	DMSO	45.1	9 [97]
5	DMF	43.8	13 [96]
6	None	–	77 [93]

[a] [**1c**/(**3**+**2** introduced)]×100.

[b] [**1c**/(**3**+**2** reacted)]×100.

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9. Montmorillonite KSF (Fluka) is a natural clay treated with sulfuric acid, showing the following chemical composition (average value): SiO_2 (54.0%), Al_2O_3 (17.0%), Fe_2O_3 (5.2%), CaO (1.5%), MgO (2.5%), Na_2O (0.4%), K_2O (1.5%); we used this catalyst from a freshly opened container since it is demonstrated that KSF clay spontaneously deactivates on standing at rt for several months.
10. Detailed analysis of reaction mixture of *ortho*-*tert*-butylphenol **1a** revealed that 70% of the starting *tert*-butyl group was transferred to toluene whereas the remaining 30% was lost as isobutylene.
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