

## Supporting Information:

### Phenol alkylation with 1-octene on solid acid catalysts

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#### Identifying the octylphenol isomers

**Background.** The alkylation of phenol by olefins over solid acid catalysts results in the formation of both O-alkylated and C-alkylated products.<sup>1</sup> In the absence of commercially available standards for octyl phenols, it was important to confirm the identity of the various alkylated products.

The mass spectra of O-alkylated phenols (phenyl ethers), *ortho*-C-alkylated phenols and *meta*-/*para*-C-alkylated phenols are quite distinct. The O-alkylated phenols have a distinctive ion at 94 *m/z*.<sup>2</sup> The fragmentation of the C-alkylated phenols depends on the alkylation position, with *ortho*-alkylated phenols having a distinctive ion at 107 *m/z*, while *meta*-/*para*-C-alkylated phenols have a distinctive ion at 121 *m/z*.<sup>3</sup> It is therefore possible to use mass spectrometry to distinguish between most of the isomers, but not between the *meta*- and *para*-alkylated phenols.

In an attempt to further distinguish between these isomers, as well as to confirm the assignments based on mass spectrometry, octyl phenols were synthesised by two different routes that were expected to give different isomer distributions.

**Experimental.** The *alkylation of phenol with 1-octene by AlCl<sub>3</sub>* was done as follows. The glassware was dried using a stream of N<sub>2</sub> and a heatgun. AlCl<sub>3</sub> (Alfa Aesar, CAS 7446-70-0) and phenol (Aldrich, +99%, CAS 108-95-2) were placed in the round bottom flask with C<sub>9</sub>-C<sub>11</sub> *n*-paraffin solvent (Sasol) and the mixture was stirred. The 1-octene (Aldrich, 98%, CAS 111-66-0) was diluted with solvent and added dropwise through a pressure equalising funnel over a time period of 90 minutes. Once the addition was completed, the reaction mixture was allowed to stir for an additional 90 minutes.

The *alkylation of phenol with 1-octene over solid phosphoric acid (SPA)* was done as follows. The phenol and 1-octene was dissolved in pentane as solvent (Associated Chemical Enterprises). This mixture and some SPA catalyst (C84/3 Eagle Picher, Süd-Chemie Sasol Catalysts) were placed in a small stainless steel batch reactor. The reaction was performed at 200°C for 6 hours under autogenous pressure.

The products were analysed by an Agilent 6890N gas chromatograph with Agilent 5973 mass selective detector (GC-MS). An HP-Pona 50 m × 200 µm × 0.5 µm methyl siloxane column (Agilent #190915-001) was used with a 100:1 split ratio. The temperature programme used was: 40°C for 5 minutes, ramping from 40°C to 300°C at 8°C per minute, and then keeping it at 300°C for 5 minutes.

**Results and discussion.** The chromatograms obtained by octylphenol synthesis over AlCl<sub>3</sub> and solid phosphoric acid (SPA) were overlaid (Figure S1). The O-alkylated phenols had a shorter residence time and was prominent in the product from SPA catalysed alkylation, but virtually absent in the product from AlCl<sub>3</sub> alkylation.

The absence of O-alkylated phenols in the product from AlCl<sub>3</sub> alkylation was expected. The alkylation of phenol using an aluminium based catalyst proceeds through the formation of an aluminium phenoxide intermediate, which facilitates the *ortho*-alkylation of phenol by olefins.<sup>4-5</sup> Since the aluminium bonds to the oxygen, O-alkylation of the phenol is hindered and phenol ether formation is limited. Isomerisation to form *ortho*-, *meta*- and *para*-substituted C-alkylated phenols readily occurs (even in the absence of a catalyst).<sup>6</sup> It was not possible to distinguish between the *meta*- and *para*-isomers. The *ortho*-isomers were surprisingly not the most abundant isomers from AlCl<sub>3</sub> catalysed alkylation. The retention times of the various alkyl phenols are listed in Table S1.

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## Literature cited

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**Table S1.** Separation of the products from the acid catalysed alkylation of phenol with 1-octene on a 50m HP-Pona column and temperature programme starting at 40°C for 5 min, then increasing from 40°C to 300°C at 8°C/min and finally keeping it at 300°C for 5 min.

Retention time (min)	Typical value ‡	Assignment
14.06	7514	phenol
23.04	5	O-alkylation (phenyl ether)
23.34	35	O-alkylation (phenyl ether)
23.59	92	O-alkylation (phenyl ether)
23.98	457	O-alkylation (phenyl ether)
24.74	3	O-alkylation (phenyl ether)
24.80	3	O-alkylation (phenyl ether)
25.18	242	<i>ortho</i> -C-alkylation ( <i>o</i> -octylphenol)
25.42	308	<i>ortho</i> -C-alkylation ( <i>o</i> -octylphenol)
25.48	11	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
25.59	5	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
25.66	7	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
25.94	12	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
26.04	750	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
26.15	11	<i>ortho</i> -C-alkylation ( <i>o</i> -octylphenol)
26.25	310	<i>ortho</i> -C-alkylation ( <i>o</i> -octylphenol)
26.31	89	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
26.62	19	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
26.69	261	<i>meta/para</i> -C-alkylation ( <i>m/p</i> -octylphenol)
31.60-34.15	<20	di-alkylated phenols

‡ SPA catalysed alkylation at 200°C for 6 hours.

**Figure S1.** Chromatograms showing the mono-alkylated products from phenol alkylation with 1-octene on solid phosphoric acid (solid line) and on  $\text{AlCl}_3$  (dashed line).

