

# Metal cation-exchanged montmorillonite ( $M^{n+}$ -mont)-catalysed aromatic alkylation with aldehydes and ketones

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The alkylation of aromatic compounds with aldehydes and ketones in the presence of a variety of metal cation-exchanged montmorillonites ( $M^{n+}$ -mont;  $M^{n+} = Zr^{4+}, Al^{3+}, Fe^{3+}, Zn^{2+}, H^+, Na^+$ ) has been investigated.  $Al^{3+}$ - and  $Zr^{4+}$ -Monts are revealed to be effective as catalysts, while no reaction takes place with  $Na^+$ -mont.  $Al^{3+}$ -Mont-catalysed alkylation of phenol with several aldehydes produces mainly or almost solely the corresponding gem-bis(hydroxyphenyl)alkanes (bisphenols) in good yields, while that with several ketones affords selectively the corresponding alkylphenols in moderate to good yields. The alkylation always occurs at the carbonyl carbon without any skeletal rearrangement and the kind of products depends much on the steric hindrance of an electrophilic intermediary carbocation. The alkylation of anisole, veratrole and *p*-cresol proceeds well, while that of toluene, benzene, chlorobenzene and nitrobenzene scarcely occurs.

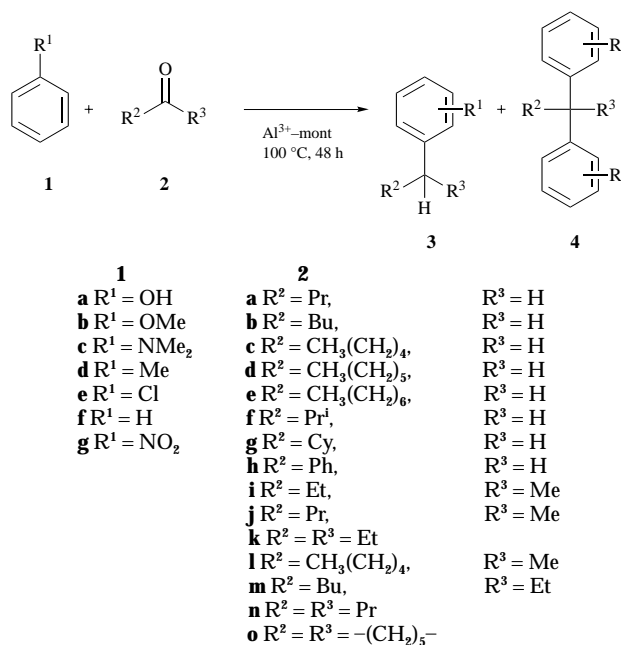
## Introduction

Selective organic transformation in the presence of various solid catalysts including metal-cation exchanged clays is of current interest in ensuring that synthetic processes are environmentally friendly.<sup>1</sup> In our course of studies on metal cation-exchanged montmorillonite ( $M^{n+}$ -mont)-catalysed organic unit reactions, we reported the  $M^{n+}$ -mont-catalysed rearrangement of 4-phenoxybutan-2-one to the corresponding alkylphenol, namely 4-(4-hydroxyphenyl)butan-2-one (raspberry ketone); we also noted the formation of a little 3,4-dihydro-4-methyl-2*H*-1-benzopyran (4-methylchroman) probably as a result of intramolecular reductive aromatic alkylation with a carbonyl moiety.<sup>2</sup> Intra- and inter-molecular aromatic alkylations with aldehydes and ketones have been less studied than the corresponding alkylations with alcohols, alkyl halides or alkenes; this is because the former reactions normally give a low yield of the expected products because of polymeric by-product formation.<sup>3</sup> Although the alkylation of phenol with aldehydes and ketones in the presence of several acid catalysts to produce gem-bis(hydroxyphenyl)alkanes (bisphenols) has been investigated, few attempts have been made to produce alkylphenols by the corresponding aromatic alkylations.<sup>4,5</sup> For example, the dry HCl-catalysed reaction of phenol with aldehydes in glacial acetic acid produced polymeric products, the pyrolysis of which gave alkylphenols in good yields by way of disproportionation.<sup>4,5</sup> Such alkylphenols and bisphenols find use in the pharmaceutical and agrochemical industries.<sup>6</sup> In view of this we have developed a facile one-pot preparative method for alkylphenols and/or bisphenols by intermolecular reductive alkylation of phenol with aldehydes and ketones using  $M^{n+}$ -monts as catalysts.<sup>7</sup>

## Results and discussion

### Alkylation of phenol **1a** with aldehydes in the presence of $M^{n+}$ -mont

Treatment of phenol **1a** with octanal **2e** in the presence of  $Al^{3+}$ -mont at 100 °C for 48 h produced 1-(hydroxyphenyl)octanes **3ae** *para*-selectively (*o*:-*p* = 8:92 estimated by GLC, 25% isolated yield) and an isomeric mixture of 1,1-bis(4-hydroxyphenyl)octane, 1-(2-hydroxyphenyl)-1-(4-hydroxyphenyl)octane and 1,1-bis(2-hydroxyphenyl)octane **4ae** (58% isolated yield, in a



Scheme 1

ratio of 5:4:1) (Scheme 1). One of the characteristic features of this reaction is that the alkylation always occurred at the carbonyl carbon without any skeletal rearrangement to give compounds **3** and **4**; thus, 2-, 3- and 4-(hydroxyphenyl)octanes and the corresponding bisphenols were not formed. This is in sharp contrast to the  $Ga_2Cl_4$ -mediated reductive Friedel-Crafts alkylation of anisole **1b** with aldehydes<sup>8</sup> and the  $AlCl_3$ -mediated reaction of **1a** with ketones,<sup>5</sup> both reactions having been reported to be accompanied by a skeletal rearrangement. The reaction similarly proceeded with  $Zr^{4+}$ -,  $Zn^{2+}$ -,  $Fe^{3+}$ - and  $H^+$ -mont (montmorillonite K10 or  $H_2SO_4$ -treated clay), but it did not occur with  $Na^+$ -mont (Kunipia<sup>®</sup> G).

Although recovered  $Al^{3+}$ -mont could not be reused for this reaction, it was successfully regenerated and reused at least three times almost without a loss of activity after being washed with 50% aqueous acetone and then dried at 120 °C.

The  $Al^{3+}$ -mont-catalysed reaction was then applied to the reaction of phenol with butanal **2a**, pentanal **2b**, hexanal **2c**,

**Table 1** Alkylation of aromatic compounds with aldehydes and ketones in the presence of  $M^{n+}$ -mont<sup>a</sup>

| Run      | Aromatic compd. | Carbonyl compd. | $M^{n+}$ -Mont                 | Products, isolated yield (%) <sup>b</sup>                  |              |   |               |
|----------|-----------------|-----------------|--------------------------------|--|--------------|---|---------------|
|          |                 |                 |                                | Alkylphenols ( <i>o</i> :- <i>p</i> - ratio <sup>c</sup> ) |              | Bisphenols (ratio of 3 isomers <sup>c</sup> ) |               |
| Aldehyde |                 |                 |                                |  |              |   |               |
| 1        | <b>1a</b>       | <b>2a</b>       | Al <sup>3+</sup> -mont         | <b>3aa</b> ,   | 6 (16:84);   | <b>4aa</b> ,                                  | 69 (6:4:<0.1) |
| 2        | <b>1a</b>       | <b>2b</b>       | Al <sup>3+</sup> -mont         | <b>3ab</b> ,   | 7 (10:90);   | <b>4ab</b> ,                                  | 75 (5:4:1)    |
| 3        | <b>1a</b>       | <b>2c</b>       | Al <sup>3+</sup> -mont         | <b>3ac</b> ,   | 11 (8:92);   | <b>4ac</b> ,                                  | 65 (5:4:1)    |
| 4        | <b>1a</b>       | <b>2d</b>       | Al <sup>3+</sup> -mont         | <b>3ad</b> ,   | 14 (7:93);   | <b>4ad</b> ,                                  | 62 (5:4:1)    |
| 5        | <b>1a</b>       | <b>2e</b>       | Al <sup>3+</sup> -mont         | <b>3ae</b> ,   | 25 (8:92);   | <b>4ae</b> ,                                  | 58 (5:4:1)    |
| 6        | <b>1a</b>       | <b>2e</b>       | Zr <sup>4+</sup> -mont         | <b>3ae</b> ,   | 15 (9:91);   | <b>4ae</b> ,                                  | 75 (5:4:1)    |
| 7        | <b>1a</b>       | <b>2e</b>       | Fe <sup>3+</sup> -mont         | <b>3ae</b> ,   | 3 (9:91);    | <b>4ae</b> ,                                  | 30 (5:4:1)    |
| 8        | <b>1a</b>       | <b>2e</b>       | Zn <sup>2+</sup> -mont         | <b>3ae</b> ,   | 0;           | <b>4ae</b> ,                                  | 61 (5:4:1)    |
| 9        | <b>1a</b>       | <b>2e</b>       | H <sup>+</sup> -mont           | <b>3ae</b> ,   | 0;           | <b>4ae</b> ,                                  | 43 (5:4:1)    |
| 10       | <b>1a</b>       | <b>2e</b>       | Na <sup>+</sup> -mont          | <b>3ae</b> ,   | 0;           | <b>4ae</b> ,                                  | 0             |
| 11       | <b>1a</b>       | <b>2f</b>       | Al <sup>3+</sup> -mont         | <b>3af</b> ,   | 10 (16:84);  | <b>4af</b> ,                                  | Trace         |
| 12       | <b>1a</b>       | <b>2g</b>       | Al <sup>3+</sup> -mont         | <b>3ag</b> ,   | 16 (16:84);  | <b>4ag</b> ,                                  | Trace         |
| 13       | <b>1a</b>       | <b>2h</b>       | Al <sup>3+</sup> -mont         | <b>3ah</b> ,   | Trace;       | <b>4ah</b> ,                                  | 90 (5:4:1)    |
| Ketone   |                 |                 |                                |  |              |   |               |
| 14       | <b>1a</b>       | <b>2i</b>       | Al <sup>3+</sup> -mont         | <b>3ai</b> ,   | 27 (22:78)   |   |               |
| 15       | <b>1a</b>       | <b>2j</b>       | Al <sup>3+</sup> -mont         | <b>3aj</b> ,   | 51 (8:92)    |   |               |
| 16       | <b>1a</b>       | <b>2j</b>       | Zr <sup>4+</sup> -mont         | <b>3aj</b> ,   | 39 (7:93)    |   |               |
| 17       | <b>1a</b>       | <b>2j</b>       | Fe <sup>3+</sup> -mont         | <b>3aj</b> ,   | 6 (7:93)     |   |               |
| 18       | <b>1a</b>       | <b>2j</b>       | Zn <sup>2+</sup> -mont         | <b>3aj</b> ,   | 0            |   |               |
| 19       | <b>1a</b>       | <b>2j</b>       | H <sup>+</sup> -mont           | <b>3aj</b> ,   | 0            |   |               |
| 20       | <b>1a</b>       | <b>2j</b>       | Na <sup>+</sup> -mont          | <b>3aj</b> ,   | 0            |   |               |
| 21       | <b>1a</b>       | <b>2k</b>       | Al <sup>3+</sup> -mont         | <b>3ak</b> ,   | 46 (0:100)   |   |               |
| 22       | <b>1a</b>       | <b>2l</b>       | Al <sup>3+</sup> -mont         | <b>3al</b> ,   | 61 (3:97)    |   |               |
| 23       | <b>1a</b>       | <b>2m</b>       | Al <sup>3+</sup> -mont         | <b>3am</b> ,   | 48 (0:100)   |   |               |
| 24       | <b>1a</b>       | <b>2n</b>       | Al <sup>3+</sup> -mont         | <b>3an</b> ,   | 27 (0:100)   |   |               |
| 25       | <b>1a</b>       | <b>2o</b>       | Al <sup>3+</sup> -mont         | <b>3ao</b> ,   | 78 (23:77)   |   |               |
| 26       | <b>1a</b>       | <b>2e</b>       | AlCl <sub>3</sub> <sup>d</sup> | <b>3ae</b> ,   | Trace;       | <b>4ae</b> ,                                  | Trace         |
| 27       | <b>1b</b>       | <b>2e</b>       | Al <sup>3+</sup> -mont         | <b>3be</b> ,   | 12 (<1:>99); | <b>4be</b> ,                                  | 25 (8:2:<0.1) |
| 28       | <b>1b</b>       | <b>2j</b>       | Al <sup>3+</sup> -mont         | <b>3bj</b> ,   | 32 (0:100);  | <b>4bj</b> ,                                  | 12 (8:2:<0.1) |
| 29       | <b>1b</b>       | <b>2o</b>       | Al <sup>3+</sup> -mont         | <b>3bo</b> ,   | 32 (3:97)    |   |               |
| 30       | <b>5</b>        | <b>2j</b>       | Al <sup>3+</sup> -mont         | <b>7</b> ,   | Trace;       | <b>8</b> ,                                    | 20            |
| 31       | <b>5</b>        | <b>2o</b>       | Al <sup>3+</sup> -mont         | <b>9</b> ,   | 30           |   |               |
| 32       | <b>6</b>        | <b>2j</b>       | Al <sup>3+</sup> -mont         | <b>10</b> ,  | 29           |   |               |

<sup>a</sup> Aromatic compound (26.6 mmol), aldehyde or ketone (0.78 mmol),  $M^{n+}$ -mont (0.266 mmol as acid sites estimated by NH<sub>3</sub>-TPD) at 100 °C for 48 h.

<sup>b</sup> Based on **2**. Bisphenol **4** is an isomeric mixture. <sup>c</sup> Estimated by GLC. <sup>d</sup> 2.66 mmol.

heptanal **2d** and benzaldehyde **2h**. As a result, the corresponding 1,1-bis(hydroxyphenyl)butanes **4aa**, 1,1-bis(hydroxyphenyl)pentanes **4ab**, 1,1-bis(hydroxyphenyl)hexanes **4ac**, 1,1-bis(hydroxyphenyl)heptanes **4ad** and 1,1-bis(hydroxyphenyl)-1-phenylmethanes **4ah** were obtained as major products together with a small amount of the corresponding alkylphenols **3** (see Table 1). Compounds **4aa**, **4ab**, **4ac**, **4ad** and **4ah** also consisted of *p,p*- (the major), *p,o*- and *o,o*-isomers, respectively. In particular, the alkylation of **1a** with **2h** produced **4ah** almost exclusively in 90% isolated yield. For comparison, all reactions were carried out with H<sup>+</sup>-mont as catalyst in place of Al<sup>3+</sup>-mont, where **4aa**, **4ab**, **4ac**, **4ad**, **4ae** and **4ah** were obtained in 60, 60, 53, 48, 43 and 21% isolated yields, respectively, no alkylphenols being produced. When phenol was treated with isobutyraldehyde **2f** and cyclohexanecarbaldehyde **2g** in the presence of Al<sup>3+</sup>-mont, the corresponding alkylphenols **3** were the major products, the corresponding bisphenols **4** being almost completely absent.

Under the present conditions AlCl<sub>3</sub> was not an effective catalyst. For example, in the alkylation of **1a** with **2e** using anhydrous AlCl<sub>3</sub> (an equivalent amount to Al<sup>3+</sup>-mont), none of the expected alkylphenol **3ae** or bisphenol **4ae** was produced. Use of an excess of AlCl<sub>3</sub> gave only very low yields of **3ae** and **4ae** accompanied by large amounts of tarry products.

#### Alkylation of the phenol **1a** with ketones in the presence of $M^{n+}$ -mont

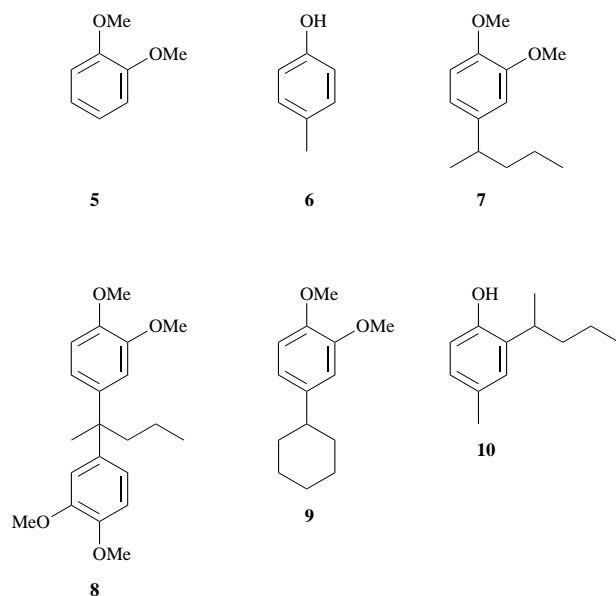
The alkylation of **1a** with ketones such as pentan-2-one **2j** and pentan-3-one **2k** produced 2-(hydroxyphenyl)pentanes **3aj** (*o*:-*p* = 8:92) in 51% isolated yield and 3-(hydroxyphenyl)-

pentane **3ak** (*o*:-*p* = 0:100) in 46% isolated yield, respectively (Scheme 1, Table 1). In this case, Al<sup>3+</sup>-mont was the most promising catalyst. Compound **3aj** was obtained only in 29% yield with Zr<sup>4+</sup>-mont, while the reaction failed to proceed at all with Zn<sup>2+</sup>-, H<sup>+</sup>- and Na<sup>+</sup>-mont. With heptan-2-one **2l**, heptan-3-one **2m** and heptan-4-one **2n** compound **1a** was similarly alkylated *para*-selectively to produce 2-(hydroxyphenyl)heptanes **3al** (*o*:-*p* = 3:97), 3-(hydroxyphenyl)heptane **3am** (*o*:-*p* = 0:100) and 4-(hydroxyphenyl)heptane **3an** (*o*:-*p* = 0:100), respectively, in moderate yield. The alkylation of **1a** with cyclohexanone **2o** afforded (hydroxyphenyl)cyclohexanes **3ao** (*o*:-*p* = 23:77) in 78% isolated yield. Typical results using ketones are also shown in Table 1. As in the case of aldehydes, the alkylation with aldehydes also occurred at the carbonyl carbon to give the corresponding alkylphenols **3**. In contrast to alkylation with aldehydes, that with ketones **2i-o** produced alkylphenols **3ai-ao** almost exclusively, little of the corresponding bisphenols **4** being detected by GC-MS early in the reaction.

The AlCl<sub>3</sub>-mediated reaction of **1a** with ketones was reported to be accompanied by a skeletal rearrangement.<sup>5</sup> Under the reported conditions (at 120 °C for 3 h) of the AlCl<sub>3</sub>-mediated reaction, however, **1a** reacted with **2j** and **2k** to give only the corresponding non-rearranged alkylphenols **3aj** and **3ak** in yields of 19% (*o*:-*p* = 8:92) and 27% (*o*:-*p* = 0:100), respectively.

#### Alkylation of aromatic compounds with aldehydes and ketones in the presence of $M^{n+}$ -mont

In the presence of Al<sup>3+</sup>-mont catalyst, the alkylation of anisole **1b** with octanal **2e** provided octylanisole **3be** (12% isolated



yield; *para*-isomer, >99%), 1,1-bis(methoxyphenyl)octanes **4be** [25% isolated yield, a mixture of 3 isomers (8:2:<0.1)] and unidentified tarry compounds. Treatment of **1b** with pentan-2-one **2j** gave (1-methylbutyl)anisole **3bj** (*o*:*p* = 0:100) and 2,2-bis(methoxyphenyl)pentanes **4bj** [a mixture of 3 isomers (8:2:<0.1)] in 32 and 12% isolated yield, respectively. However, on reaction with cyclohexanone **2o** **1b** produced the cyclohexylanisoles **3bo** (*o*:*p* = 3:97) in 32% isolated yield. Similarly, veratrole **5** reacted with pentan-2-one **2j** to give 2,2-bis(3,4-dimethoxyphenyl)pentane **8** in 19% isolated yield, while it gave only 1-cyclohexyl-3,4-dimethoxybenzene **9** in 20% isolated yield on reaction with **5**. The reaction of *p*-cresol **6** with pentan-2-one **2j** produced 4-methyl-2-(1-methylbutyl)phenol **10** in 29% isolated yield, whilst it failed to react with **2o**. The reaction of toluene **1d** with **2e** or **2o** was very sluggish to give only a trace of products, whilst with chlorobenzene **1e**, benzene **1f** and nitrobenzene **1g** there was no reaction. Treatment of *N,N*-dimethylaniline and *N,N*-diethylaniline with a variety of ketones and aldehydes under similar conditions gave little of the expected alkylated products, diarylmethanes and diaryl-ethanes being the only identifiable and major compounds. Such compounds were produced in similar yields (10–20% based on anilines) even in the absence of carbonyl compounds. Similar reactions have been recorded with clay catalysts.<sup>9</sup>

#### Plausible reaction pathway

We confirmed separately that the bisphenols **4aa**, **4ae** and 2,2-bis(4-hydroxyphenyl)propane (commercially available bisphenol A) were not converted into the corresponding alkylphenols **3** under the present reaction conditions (in phenol) and that the bisphenol **4aa** and bisphenol A were not produced by treatment of **1a** with 1-(hydroxyphenyl)butanes **3aa** and 2-(4-hydroxyphenyl)propane, respectively. However, in the case of Al<sup>3+</sup>-mont-catalysed aromatic alkylation of phenol **1a** with **2a** in the presence of **4aa**, the yield of **3aa** increased. These results suggested that the alkylphenols **3** and bisphenols **4** might be produced competitively. The plausible course of the reaction is shown schematically in Scheme 2 with phenol as an aromatic substrate. An intermediary carbocation **I** may be formed by the effect of the Lewis acid sites of Al<sup>3+</sup>-mont, although M<sup>n+</sup>-monts have both Brønsted and Lewis acid sites.<sup>10</sup> Such a carbocation could be stabilised by negatively charged oxygen atoms in the interlayer space of Al<sup>3+</sup>-mont (between two silicate sheets of Al<sup>3+</sup>-mont), and then either react with **1a** electrophilically to produce **4** or possibly abstract a hydride<sup>11,12</sup> from the bisphenols **4** or some other species to produce **3** competitively. The secondary carbocations **I** produced from aldehydes might react

with phenol and abstract a hydride much faster than the tertiary carbocations **I** obtained from ketones. However, the experimental results of the product distribution show that the steric hindrance of **I** might control the kind of products in this inter-layer reaction, and thus, the reaction rate between less hindered secondary carbocations and phenol might be less affected than that between tertiary carbocations and phenol, although the details are not yet known.

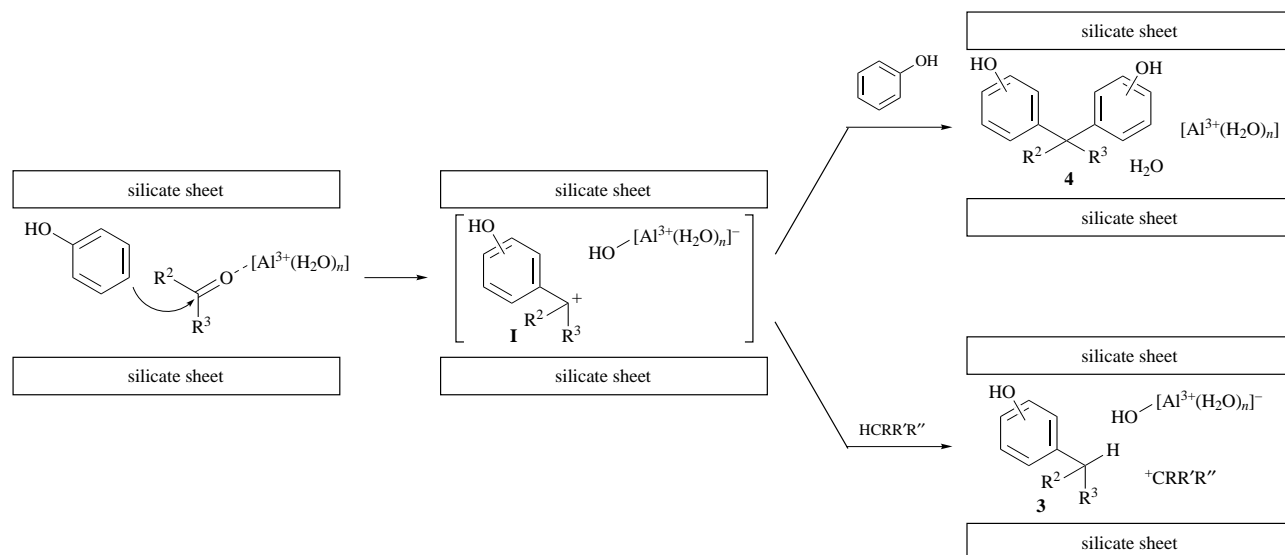
#### Conclusion

Al<sup>3+</sup>-, Zr<sup>4+</sup> and Fe<sup>3+</sup>-Monts-catalysed aromatic alkylation of phenol **1a** with aldehydes gave the corresponding bisphenols [gem-bis(hydroxyphenyl)alkanes] **4** either mainly or almost exclusively in good yields; similar reactions with ketones afforded selectively the corresponding alkylphenols **3** in moderate to good yields. The alkylation always occurred at the carbonyl carbon without any skeletal rearrangement and the kind of products was greatly dependent on the steric hindrance in the electrophilic intermediary carbocation. The catalyst was re-used several times after being washed and dried. The alkylation of anisole **1b**, veratrole **5** and *p*-cresol **6** proceeded similarly to produce mainly the corresponding alkylphenols **3** in moderate yields; under the present conditions such alkylations failed with unactivated aromatic compounds such as toluene, benzene, chlorobenzene and nitrobenzene.

#### Experimental

NMR spectra were recorded on JEOL EX-400 (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C NMR, 100 MHz) and JEOL GSX-270 (<sup>1</sup>H NMR, 270 MHz; <sup>13</sup>C NMR, 67.8 MHz) instruments for solutions in CDCl<sub>3</sub> or [<sup>2</sup>H<sub>6</sub>]acetone with Me<sub>4</sub>Si as an internal standard. Coupling constants *J* are given in Hz; abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were measured on a Shimadzu QP-5000S mass spectrometer equipped with a Shimadzu GC-17 gas-liquid chromatograph (30 m × 0.254 mm, 0.25 μm film thickness, J&W Scientific fused silica capillary column DB-1). The electron-impact method was used for ionisation, the ionising voltage being 70 eV for all compounds. High resolution mass spectra (HRMS) were obtained on a JEOL JMS SX-102A instrument. The electron-impact method was used for ionisation, the ionising voltage being 75 eV for all compounds. GLC analyses were performed on a Shimadzu GC-14A instrument (25 m × 0.33 mm, 5.0 μm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionisation detectors and helium as carrier gas and on a Shimadzu GC-14A instrument (2 m × 3 mm glass column packed with 5% OV<sup>®</sup>-17 on Chromosorb<sup>®</sup> W) with flame-ionisation detectors and nitrogen as carrier gas. Recycling preparative high performance liquid chromatography (HPLC) was performed on a JAI LC-908-G30 instrument (600 mm × 20 mm × 2, JAIGEL-1H and JAIGEL-2H dual styrene polymer columns) equipped with ultraviolet (UV) and refractive-index (RI) detectors and CHCl<sub>3</sub> as an eluent. Column chromatography on SiO<sub>2</sub> was performed with Wakogel<sup>®</sup> C-300 using hexane, hexane-ethyl acetate and ethyl acetate as eluents. Melting points were determined on a Yanaco MP-S3 micro melting-point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

All commercially available organic and inorganic compounds were used without further purification except for the solvent, which was dried and distilled by the known method before use.<sup>13</sup> Montmorillonite K10, namely H<sup>+</sup>-mont, was commercially available from the Aldrich Chemical Co., Inc., which was used as obtained. Kunipia<sup>®</sup> G, namely Na<sup>+</sup>-mont, was obtained from Kunimine Industries Co., Ltd. M<sup>n+</sup>-Mont (M<sup>n+</sup> = Zr<sup>4+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>) was prepared by treatment of Na<sup>+</sup>-mont with the corresponding metal oxychloride or nitrate



Scheme 2

in aqueous acetone as described previously.<sup>14</sup> *ortho*- and/or *para*-Alkylphenols **3aa**,<sup>15</sup> **3ab**,<sup>15</sup> **3ac**,<sup>15</sup> **3ad**,<sup>16</sup> **3ae**,<sup>15</sup> **3af**,<sup>17</sup> **3ag**,<sup>18,19</sup> **3ai**,<sup>20</sup> **3aj**,<sup>21</sup> **3ak**,<sup>22</sup> **3al**,<sup>23,24</sup> **3am**,<sup>24</sup> **3an**,<sup>24</sup> **3ao**,<sup>25</sup> **3be**,<sup>26</sup> **3bj**,<sup>21</sup> **3bo**,<sup>27</sup> **4bj**,<sup>28</sup> **9**<sup>29</sup> and **10**<sup>30</sup> are known compounds and were characterised from spectral data. New spectral data for the compounds are shown below. The compounds **4aa**, **4ab**, **4ac**, **4ad**, **4ae**, **4ah**, **4be** and **8** are new and were characterised from their mass spectral data (GC-MS and HRMS) and combustion analytical data. All bisphenols are unstable in air and the initial colourless or pale yellow coloured oil changed gradually to pale-red oils and/or tarry compounds. Therefore, it was sometimes difficult to obtain correct combustion analytical data.

#### General procedure for $M^{3+}$ -mont-catalysed alkylation of aromatic compound with aldehydes or ketones

As a typical example, alkylation of phenol **1a** with octanal **2e** in the presence of  $Al^{3+}$ -mont is described below (Table 1, run 5). To **1a** (2.50 g, 26.6 mmol) in a 20 cm<sup>3</sup> two-necked pear-shaped flask equipped with an Allihn condenser with a silica gel tube was added  $Al^{3+}$ -mont (white powder; 500 mg, 0.266 mmol as acid sites estimated by  $NH_3$ -TPD<sup>2</sup>) at ca. 40 °C with magnetic stirring. The mixture was heated to 100 °C during ca. 15 min and kept at this temperature for ca. 45 min. The aldehyde **2e** (100 mg, 0.78 mmol) was added dropwise to the mixture which was then stirred vigorously for 48 h at 100 °C. After the mixture had been cooled, the catalyst was filtered off and rinsed with diethyl ether (20 cm<sup>3</sup>). Removal of unchanged **1a** and **2e** and ether by distillation under reduced pressure left a brown oil which was subjected to column chromatography (Wakogel<sup>®</sup> C-300, eluents: hexane, hexane-ethyl acetate and ethyl acetate) and bulb-to-bulb distillation. The products were a colourless oil of 1-(hydroxyphenyl)octanes **3ae** (hexane-ethyl acetate as an eluent; 40.2 mg, 25% isolated yield, *o* : *p* = 8 : 92 determined by GLC) and a pale yellow oil of 1,1-bis(hydroxyphenyl)octanes **4ae** [hexane-ethyl acetate and ethyl acetate as eluents; 135.1 mg, 58% isolated yield; a mixture of three isomers of ca. 5 : 4 : 1 ratio in GLC; isolated by recycling preparative HPLC successively and assigned by <sup>13</sup>C NMR spectra and GC-MS as 1,1-bis(4-hydroxyphenyl)octanes, 1-(2-hydroxyphenyl)-1-(4-hydroxyphenyl)octanes and 1,1-bis(2-hydroxyphenyl)octanes, respectively]. The isomers of other bisphenols were similarly assigned by <sup>13</sup>C NMR spectral and mass spectral (GC-MS and HRMS) results and combustion analyses.

**1,1-Bis(hydroxyphenyl)butanes 4aa.** A pale yellow oil (isomer ratio 6 : 4 : <0.1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)butane as a major component isolated by successive

recycling preparative HPLC and identified by <sup>13</sup>C NMR and mass spectra (GC-MS); a pale-yellow crystalline solid;  $\delta_C$  (100 MHz) 14.0 (q), 21.1 (t), 38.2 (t), 49.3 (d), 115.1 (d), 128.8 (d), 138.0 (s) and 153.6 (s); *m/z* 242 ( $M^+$ , 8%) and 199 (100) (Found: *m/z* 242.1298.  $C_{16}H_{18}O_2$  requires *m/z* 242.1307) as a mixture of isomers (Found: C, 78.68; H, 7.42%.  $C_{16}H_{18}O_2$  requires C, 79.31; H, 7.49%).

**1,1-Bis(hydroxyphenyl)pentanes 4ab.** A pale yellow oil (isomer ratio 5 : 4 : 1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)pentane as a major component isolated by successive recycling preparative HPLC and identified by <sup>13</sup>C NMR and mass spectroscopy (GC-MS); a pale-yellow crystalline solid;  $\delta_C$  (100 MHz) 14.0 (q), 22.7 (t), 30.2 (t), 35.8 (t), 49.6 (d), 115.2 (d), 128.9 (d), 138.1 (s) and 153.5 (s); *m/z* 256 ( $M^+$ , 7%) and 199 (100) (Found: *m/z* 256.1464.  $C_{17}H_{20}O_2$  requires *m/z* 256.1463) (Found: C, 79.10; H, 7.87%.  $C_{17}H_{20}O_2$  requires C, 79.65; H, 7.86%).

**1,1-Bis(hydroxyphenyl)hexanes 4ac.** A pale yellow oil (isomer ratio 5 : 4 : 1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)hexane as a major component isolated by successive recycling preparative HPLC and identified by <sup>13</sup>C NMR and mass spectroscopy (GC-MS); a pale-yellow crystalline solid;  $\delta_C$  (100 MHz) 14.1 (q), 22.5 (t), 27.7 (t), 31.9 (t), 36.1 (t), 49.6 (d), 115.2 (d), 128.9 (d), 138.1 (s) and 153.6 (s); *m/z* 270 ( $M^+$ , 5%) and 199 (100) (Found: *m/z* 270.1632.  $C_{18}H_{22}O_2$  requires *m/z* 270.1620) (Found: C, 79.22; H, 8.28%.  $C_{18}H_{22}O_2$  requires C, 79.96; H, 8.20%).

**1,1-Bis(hydroxyphenyl)heptanes 4ad.** A pale yellow oil (isomer ratio 5 : 4 : 1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)heptane as a major component isolated by successive recycling preparative HPLC and identified by <sup>13</sup>C NMR and mass spectroscopy (GC-MS); a pale-yellow crystalline solid;  $\delta_C$  (100 MHz) 14.1 (q), 22.6 (t), 28.0 (t), 29.3 (t), 31.7 (t), 36.1 (t), 49.6 (d), 115.2 (d), 128.8 (d), 138.1 (s) and 153.6 (s); *m/z* 284 ( $M^+$ , 4%) and 199 (100) (Found: *m/z* 284.1780.  $C_{19}H_{24}O_2$  requires *m/z* 284.1776) (Found: C, 79.64; H, 8.35%.  $C_{19}H_{24}O_2$  requires C, 80.24; H, 8.51%).

**1,1-Bis(hydroxyphenyl)octanes 4ae.** A pale yellow oil (isomer ratio 5 : 4 : 1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)octane as a major component isolated by successive recycling preparative HPLC and identified by <sup>13</sup>C NMR and mass spectroscopy (GC-MS); a pale-yellow crystalline solid;  $\delta_C$  (100 MHz) 14.1 (q), 22.6 (t), 28.0 (t), 29.2 (t), 29.6 (t), 31.9 (t), 36.1

(t), 49.6 (d), 115.2 (d), 128.8 (d), 138.1 (s) and 153.6 (s);  $m/z$  298 ( $M^+$ , 3%) and 199 (100) (Found:  $m/z$  298.1934.  $C_{20}H_{26}O_2$  requires  $m/z$  298.1933) (Found: C, 79.17; H, 8.73%.  $C_{20}H_{26}O_2$  requires C, 80.05; H, 8.78%).

**1,1-Bis(hydroxyphenyl)-1-phenylmethanes 4ah.** A pale yellow oil (isomer ratio 5:4:1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-hydroxyphenyl)-1-phenylmethane as a major component isolated by successive recycling preparative HPLC and identified by  $^{13}C$  NMR and mass spectroscopy (GC-MS); a pale-yellow crystalline solid;  $\delta_C$ (100 MHz,  $[^2H_6]$ acetone) 55.9 (d), 115.7 (d), 126.6 (d), 128.8 (d), 129.9 (d), 130.9 (d), 136.2 (s), 146.0 (s) and 156.4 (s);  $m/z$  276 ( $M^+$ , 100%), 199 (85) and 181 (91) (Found:  $m/z$  276.1150.  $C_{19}H_{16}O_2$  requires  $m/z$  276.1150) (Found: C, 81.35; H, 5.73%.  $C_{19}H_{16}O_2$  requires C, 82.58; H, 5.84%).

**1,1-Bis(methoxyphenyl)octanes 4be.** A pale yellow oil (isomer ratio 8:2:<0.1) was characterised by mass spectroscopy (GC-MS and HRMS) and combustion analysis; 1,1-bis(4-methoxyphenyl)octane as a major component isolated by successive recycling preparative HPLC and identified by  $^{13}C$  NMR and mass spectroscopy (GC-MS); a colourless oil;  $\delta_C$ (100 MHz) 14.1 (q), 22.7 (t), 28.1 (t), 29.2 (t), 29.6 (t), 31.9 (t), 36.1 (t), 49.6 (d), 55.2 (q), 113.7 (d), 128.6 (d), 138.0 (s) and 157.7 (s);  $m/z$  326 ( $M^+$ , 3%) and 227 (100) (Found:  $m/z$  326.2244.  $C_{22}H_{30}O_2$  requires  $m/z$  326.2246) (Found: C, 80.95; H, 9.52%.  $C_{22}H_{30}O_2$  requires C, 80.94; H, 9.26%).

**2,2-Bis(3,4-dimethoxyphenyl)pentane 8.** A pale yellow oil was isolated by successive recycling preparative HPLC and characterised by  $^{13}C$  NMR spectroscopy, mass spectroscopy (GC-MS) and combustion analysis;  $\delta_C$ (67.8 MHz) 14.1 (q), 18.1 (t), 28.0 (q), 44.5 (t), 45.7 (s), 55.7 (q), 55.8 (q), 110.3 (d), 111.3 (d), 119.1 (d), 142.6 (s), 146.8 (s) and 148.3 (s);  $m/z$  344 ( $M^+$ , 12%) and 301 (100) (Found: C, 72.68; H, 8.09%.  $C_{21}H_{28}O_4$  requires C, 73.23; H, 8.19%).

**1-(Hydroxyphenyl)butanes 3aa.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)butane as a major component,  $\delta_H$ (270 MHz) 0.91 (3H, t,  $J$ 7.6), 1.34 (2H, sextet,  $J$ 7.6), 1.55 (2H, quintet,  $J$ 7.6), 2.53 (2H, t,  $J$ 7.6), 4.70 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 7.34 (2H, d,  $J$ 8.3);  $m/z$  150 ( $M^+$ , 12%) and 107 (100).

**1-(Hydroxyphenyl)pentanes 3ab.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)pentane as a major component,  $\delta_H$ (400 MHz) 0.89 (3H, t,  $J$ 7.2), 1.26–1.34 (4H, m), 1.57 (2H, quintet,  $J$ 7.6), 2.53 (2H, t,  $J$ 7.6), 4.59 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 7.04 (2H, d,  $J$ 8.3);  $m/z$  164 ( $M^+$ , 10%) and 107 (100).

**1-(Hydroxyphenyl)hexanes 3ac.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)hexane as a major component,  $\delta_H$ (400 MHz) 0.86 (3H, t,  $J$ 6.8), 1.20–1.30 (6H, m), 1.56 (2H, quintet,  $J$ 7.6), 2.50 (2H, t,  $J$ 7.6), 4.68 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 7.04 (2H, d,  $J$ 8.3);  $m/z$  178 ( $M^+$ , 8%) and 107 (100).

**1-(Hydroxyphenyl)heptanes 3ad.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)heptane as a major component,  $\delta_H$ (400 MHz) 0.88 (3H, t,  $J$ 6.8), 1.19–1.30 (8H, m), 1.56 (2H, quintet,  $J$ 7.7), 2.53 (2H, t,  $J$ 7.7), 4.67 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 7.04 (2H, d,  $J$ 8.3);  $m/z$  192 ( $M^+$ , 7%) and 107 (100).

**1-(Hydroxyphenyl)octanes 3ae.** A pale yellow oil characterised by  $^1H$  NMR,  $^{13}C$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)octane as a major component,  $\delta_H$ (400 MHz) 0.87 (3H, t,  $J$ 7.3), 1.20–1.35 (10H, m), 1.56 (2H, m), 2.52 (2H, t,  $J$ 7.3), 5.24 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 7.02 (2H, d,  $J$ 8.3);  $\delta_C$ (100 MHz) 14.1 (q), 22.7 (t), 29.3 (t), 29.3 (t), 29.5 (t), 31.7 (t), 31.9 (t), 35.1 (t), 115.1 (d), 129.4 (d), 135.2 (s) and 153.3 (s);  $m/z$  206 ( $M^+$ , 11%) and 107 (100).

**1-(Hydroxyphenyl)-2-methylpropanes 3af.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)-2-methylpropane as a major component,  $\delta_H$ (270 MHz) 0.88 (6H, d,  $J$ 6.6), 1.72–1.86 (1H, m), 2.40 (2H, d,  $J$

7.1), 4.60 (1H, br s), 6.77 (2H, d,  $J$ 8.2) and 7.26 (2H, d,  $J$ 8.2);  $m/z$  150 ( $M^+$ , 21%), 135 (100) and 107 (52).

**(Hydroxyphenyl)methylcyclohexanes 3ag.** A pale yellow oil identified by  $^1H$  NMR and mass spectroscopy (GC-MS).<sup>18,19</sup>

**2-(Hydroxyphenyl)butanes 3ai.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 2-(4-hydroxyphenyl)butane as a major component,  $\delta_H$ (270 MHz) 0.80 (3H, t,  $J$ 7.1), 2.00 (3H, d,  $J$ 7.1), 1.55 (2H, quintet,  $J$ 7.1), 2.53 (1H, sextet,  $J$ 7.1), 4.83 (1H, br s), 6.76 (2H, d,  $J$ 8.8) and 7.38 (2H, d,  $J$ 8.8);  $m/z$  150 ( $M^+$ , 11%) and 121 (100).

**2-(Hydroxyphenyl)pentanes 3aj.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 2-(4-hydroxyphenyl)pentane as a major component,  $\delta_H$ (270 MHz) 0.85 (3H, t,  $J$ 7.0), 1.19 (3H, d,  $J$ 7.0), 1.12–1.29 (2H, m), 1.50 (2H, q,  $J$ 7.0), 2.63 (1H, sextet,  $J$ 7.0), 4.80 (1H, br s), 6.75 (2H, d,  $J$ 8.4) and 7.04 (2H, d,  $J$ 8.4);  $m/z$  164 ( $M^+$ , 11%) and 121 (100).

**3-(Hydroxyphenyl)pentanes 3ak.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 3-(4-hydroxyphenyl)pentane as a major component,  $\delta_H$ (400 MHz) 0.75 (6H, t,  $J$ 7.4), 1.42–1.55 (2H, m), 1.59–1.71 (2H, m), 2.24 (1H, tt,  $J$ 9.3, 5.4), 4.88 (1H, br s), 6.76 (2H, d,  $J$ 8.5) and 6.99 (2H, d,  $J$ 8.5);  $m/z$  164 ( $M^+$ , 12%), 135 (86) and 107 (100).

**2-(Hydroxyphenyl)heptanes 3al.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 2-(4-hydroxyphenyl)heptane as a major component,  $\delta_H$ (400 MHz) 0.84 (3H, t,  $J$ 6.8), 1.19 (3H, d,  $J$ 7.2), 1.21–1.28 (6H, m), 1.50 (2H, q,  $J$ 7.2), 2.60 (1H, sextet,  $J$ 7.2), 5.02 (1H, br s), 6.75 (2H, d,  $J$ 8.3) and 7.03 (2H, d,  $J$ 8.3);  $m/z$  192 ( $M^+$ , 6%), 121 (100) and 107 (13).

**3-(Hydroxyphenyl)heptanes 3am.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 3-(4-hydroxyphenyl)heptane as a major component,  $\delta_H$ (400 MHz) 0.75 (3H, t,  $J$ 7.3), 0.82 (3H, t,  $J$ 7.3), 1.03–1.14 (2H, m), 1.15–1.27 (2H, m), 1.41–1.52 (2H, m), 1.53–1.67 (2H, m), 2.30 (1H, m), 4.56 (1H, br s), 6.74 (2H, d,  $J$ 8.3) and 6.98 (2H, d,  $J$ 8.3);  $m/z$  192 ( $M^+$ , 7%), 163 (10), 135 (42) and 107 (100).

**4-(Hydroxyphenyl)heptanes 3an.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 4-(4-hydroxyphenyl)heptane as a major component,  $\delta_H$ (400 MHz) 0.83 (6H, t,  $J$ 7.3), 1.08–1.17 (4H, m), 1.39–1.54 (4H, m), 2.45 (1H, m,  $J$ 7.3), 4.57 (1H, br s), 6.75 (2H, d,  $J$ 8.3) and 7.00 (2H, d,  $J$ 8.3);  $m/z$  192 ( $M^+$ , 4%), 149 (19) and 107 (100).

**(Hydroxyphenyl)cyclohexanes 3ao.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); (4-hydroxyphenyl)cyclohexane as a major component,  $\delta_H$ (270 MHz) 1.33–1.40 (4H, m), 1.78–1.88 (6H, m), 2.29–2.38 (1H, m), 4.59 (1H, br s), 6.75 (2H, d,  $J$ 8.3) and 7.07 (2H, d,  $J$ 8.3);  $m/z$  176 ( $M^+$ , 34%), 133 (100), 120 (45) and 107 (46).

**1-(Methoxyphenyl)octanes 3be.** A pale yellow oil characterised by  $^1H$  NMR,  $^{13}C$  NMR and mass spectroscopy (GC-MS); 1-(4-methoxyphenyl)octane as a major component,  $\delta_H$ (400 MHz) 0.88 (3H, t,  $J$ 7.3), 1.20–1.35 (10H, m), 1.52–1.62 (2H, m), 2.54 (2H, t,  $J$ 7.3), 3.78 (3H, s), 6.82 (2H, d,  $J$ 8.3) and 7.09 (2H, d,  $J$ 8.3);  $\delta_C$ (100 MHz) 14.1 (q), 22.7 (t), 29.3 (t), 29.3 (t), 29.5 (t), 31.8 (t), 31.9 (t), 35.1 (t), 55.2 (q), 113.6 (d), 129.2 (d), 135.1 (s) and 157.6 (s);  $m/z$  220 ( $M^+$ , 11%) and 121 (100).

**2-(Methoxyphenyl)pentanes 3bj.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); 1-(4-hydroxyphenyl)pentane as a major component,  $\delta_H$ (270 MHz) 0.83 (3H, t,  $J$ 7.3), 1.15–1.29 (2H, m), 1.20 (3H, d,  $J$ 7.3), 1.50 (2H, q,  $J$ 7.3), 2.65 (1H, sextet,  $J$ 7.3), 3.79 (3H, s), 6.83 (2H, d,  $J$ 8.5) and 7.10 (2H, d,  $J$ 8.5);  $m/z$  178 ( $M^+$ , 15%) and 135 (100).

**(Methoxyphenyl)cyclohexanes 3bo.** A pale yellow oil characterised by  $^1H$  NMR and mass spectroscopy (GC-MS); (4-methoxyphenyl)cyclohexane as a major component,  $\delta_H$ (270 MHz) 1.31–1.42 (4H, m), 1.80–1.90 (6H, m), 2.39–2.49 (1H, m), 3.77 (3H, s), 6.83 (2H, d,  $J$ 8.5) and 7.12 (2H, d,  $J$ 8.5);  $m/z$  190 ( $M^+$ , 55%), 147 (100) and 121 (56).

**2,2-Bis(methoxyphenyl)pentanes 4bj.** A pale yellow oil charac-

terised by  $^1\text{H}$  NMR and mass spectroscopy (GC-MS); 1,1-bis(4-methoxyphenyl)pentanes as a major component,  $\delta_{\text{H}}$  (270 MHz) 0.87 (3H, t, *J* 7.3), 1.10 (2H, m), 1.57 (3H, s), 2.00 (2H, m), 3.78 (6H, s), 6.79 (4H, d, *J* 9.1) and 7.10 (4H, d, *J* 9.1);  $\delta_{\text{C}}$  (100 MHz) 14.8 (q), 18.1 (t), 28.0 (q), 44.6 (t), 45.0 (s), 55.2 (q), 113.2 (d), 128.2 (d), 142.4 (s) and 157.3 (s); *m/z* 284 ( $\text{M}^+$ , 5%) and 241 (100).

**(3,4-Dimethoxyphenyl)cyclohexane 9.** A pale yellow oil characterised by  $^1\text{H}$  NMR and mass spectroscopy (GC-MS);  $\delta_{\text{H}}$  (270 MHz) 1.35–1.44 (4H, m), 1.82–1.89 (6H, m), 2.39–2.50 (1H, m), 3.86 (3H, s), 3.88 (3H, s) and 6.74–6.79 (3H, m); *m/z* 220 ( $\text{M}^+$ , 100%), 177 (58) and 151 (36).

**2-(2-Hydroxy-5-methylphenyl)pentane 10.** A pale yellow oil characterised by  $^1\text{H}$  NMR and mass spectroscopy (GC-MS);  $\delta_{\text{H}}$  (270 MHz) 0.89 (3H, t, *J* 7.1), 1.22 (3H, d, *J* 7.1), 1.25–1.37 (2H, m), 1.56 (2H, q, *J* 7.1), 2.27 (3H, s), 3.02 (1H, sextet, *J* 7.1), 4.52 (1H, br s), 6.64 (1H, d, *J* 8.0), 6.84 (1H, d, *J* 8.0) and 6.95 (1H, s); *m/z* 178 ( $\text{M}^+$ , 15%), 135 (100) and 121 (17).

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