Al^{3+}-Exchanged Montmorillonite as an Effective Solid Catalyst for Selective Synthesis of Alkylphenols and Bisphenols

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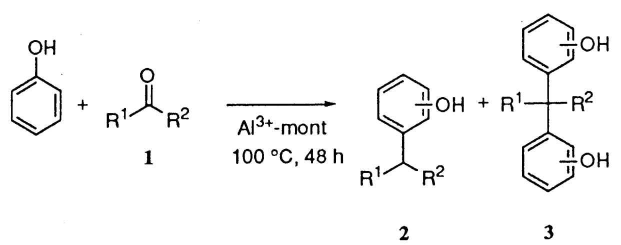
Al^{3+}-Exchanged montmorillonite-catalyzed aromatic alkylation of phenol with aldehydes produces the corresponding bisphenols mainly or almost solely in good yields, while that with ketones affords selectively the corresponding alkylphenols in moderate to good yields, the alkylation always occurring at the carbonyl carbon.

We are currently interested in the catalytic use of a variety of clays such as metal-exchanged montmorillonite (abbreviated as M^{n+}-mont)[1] and fluorotetrasilicic mica (M^{n+}-TSM)[2] in organic synthesis. During the course of our study of Al^{3+}-mont-catalyzed rearrangement of 4-phenoxybutan-2-one to the corresponding alkylphenol, 4-(4-hydroxyphenyl)butan-2-one (raspberry ketone), we observed the formation of a slight amount of 4-methylchroman probably due to an intramolecular reductive aromatic alkylation with a carbonyl moiety.[1c] Although the alkylation of phenol with aldehydes and ketones in the presence of several acid catalysts to produce bisphenols has been much investigated,[3] only a few attempts have been made on the aromatic alkylation with aldehydes and ketones to produce alkylphenols under rather stringent conditions.[4,5] These facts prompted us to develop a facile one-pot preparative method for obtaining alkylphenols and/or bisphenols [bis(hydroxyphenyl)methanes] by the intermolecular reductive alkylation of phenol with aldehydes and ketones using M^{n+}-mont as a catalyst. Preliminary results are reported here.



a ; R^1 = Pr, R^2 = H
b ; R^1 = Bu, R^2 = H
c ; R^1 = $CH_3(CH_2)_5$, R^2 = H
d ; R^1 = $CH_3(CH_2)_6$, R^2 = H
e ; R^1 = Ph, R^2 = H
f ; R^1 = Pr, R^2 = Me
g ; R^1 = R^2 = Et
h ; R^1 = $CH_3(CH_2)_4$, R^2 = Me
i ; R^1 = Bu, R^2 = Et
j ; R^1, R^2 = $-(CH_2)_5-$

Scheme 1.

Table 1. Alkylation of phenol with aldehydes and ketones[a]

Alkylating agent	Products, yield/%[b] (*o*- : *p*- ratio[c])	(ratio of 3 isomers[c])
1a	2a, 6 (16 : 84);	3a, 69 (6 : 4 : trace)
1b	2b, 7 (10 : 90);	3b, 75 (5 : 4 : 1)
1c	2c, 14 (7 : 93);	3c, 62 (5 : 4 : 1)
1d	2d, 25 (8 : 92);	3d, 58 (5 : 3 : 2)
1e	2e, trace;	3e, 90 (5 : 4 : 1)
1f	2f, 51 (8 : 92)	
1g	2g, 46 (0 : 100)	
1h	2h, 61 (3 : 97)	
1i	2i, 48 (0 : 100)	
1j	2j, 78 (23 : 77)	
1d[d]	2d, trace;	3d, trace

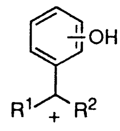
[a] Alkylating agent (0.78 mmol), phenol (26.6 mmol), Al^{3+}-mont (500 mg, 0.266 mmol) at 100 °C for 48 h. [b] Isolated yield based on the alkylating agent. All compounds gave C and H analyses within 0.30% of theory, and NMR spectra and M^+ *m/z* signals of substantial intensity in their mass spectra are consistent with their structures. The bisphenol 3 is an isomeric mixture; see Ref. 6. [c] Estimated by GLC. [d] $AlCl_3$ (2.66 mmol) was used in place of Al^{3+}-mont.

Treatment of phenol with octanal **1d** in the presence of Al^{3+}-mont[1] at 100 °C for 48 h produced 1-(hydroxyphenyl)octanes **2d** *para*-selectively (*o*- : *p*- = 8 : 92 estimated by GLC, 25% isolated yield) and an isomeric mixture of 1,1-bis(hydroxyphenyl)octanes **3d** (58% isolated yield) (Scheme 1).[6] One of the characteristic features of this reaction is that the alkylation always occurred only at the carbonyl carbon to give the compounds **2** and **3**; namely, 2-, 3- and 4-(hydroxyphenyl)octanes were not formed at all. This is in sharp contrast to the Ga_2Cl_4-mediated reductive Friedel–Crafts alkylation of anisole with aldehydes[7] and the $AlCl_3$-mediated reaction of phenol with ketones,[5] both reactions being reported to be accompanied by a skeletal rearrangement.[8] The reaction also proceeded with Zr^{4+}-mont (15% and 75%, respectively), Zn^{2+}-mont (0% and 61%), Fe^{3+}-mont (3% and 30%) and H^+-mont (montmorillonite K10) (0% and 43%), but it did not occur with Na^+-mont (Kunipia G). The reaction using Al^{3+}-mont was then applied to other aldehydes **1a** ~ **1c** and **1e**. As a result, the corresponding bisphenols **3a** ~ **3c** and **3e** were obtained as major products together with a small amount of alkylphenols **2** as shown in Table 1. Especially, the alkylation of phenol with benzaldehyde **1e** produced 1,1-bis(hydroxyphenyl)-1-phenylmethanes **3e** almost solely in 90% isolated yield. For comparison, the alkylation of phenol with the aldehyde **1d** was carried out using anhydrous $AlCl_3$ (an equivalent amount to Al^{3+}-

mont), but the expected alkylphenols **2d** and bisphenols **3d** were not produced. By use of an excess of $AlCl_3$, **2d** and **3d** were obtained only in very low yields and the reaction was accompanied by the formation of lots of tarry compounds.

On the other hand, the aromatic alkylation of phenol with ketones such as pentan-2-one **1f** and pentan-3-one **1g** produced 2-(hydroxyphenyl)pentanes **2f** (*o*- : *p*- = 8 : 92) in 51% isolated yield and 3-(hydroxyphenyl)pentanes **2g** (*o*- : *p*- = 0 : 100) in 46% isolated yield, respectively (Scheme 1, Table 1). Here, Al^{3+}-mont was most promising and, thus, with Zr^{4+}-mont **2f** was obtained only in 29% yield and no reaction occurred with Zn^{2+}-mont, H^+-mont, and Na^+-mont. With heptan-2-one **1h** and heptan-3-one **1i**, phenol was similarly alkylated *para*-selectively to produce 2-(hydroxyphenyl)heptanes **2h** (*o*- : *p*- = 3 : 97) and 3-(hydroxyphenyl)heptanes **2i** (*o*- : *p*- = 0 : 100), respectively. The alkylation of phenol with cyclohexanone **1j** afforded (hydroxyphenyl)cyclohexanes **2j** (*o*- : *p*- = 23 : 77) in 78% isolated yield. Typical results using ketones are also shown in Table 1.[9] In contrast to the cases of aldehydes, alkylation with ketones **1f** ~ **1j** produced alkylphenols **2f** ~ **2j** almost selectively.

We confirmed separately that bisphenols **3a** and **3d** and 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) were not converted to the corresponding alkylphenols **2** in phenol under the present reaction conditions and also that the bisphenol **3a** and the bisphenol A were not produced by treatment of phenol with 1-(4-hydroxyphenyl)butane and 2-(4-hydroxyphenyl)propane, respectively. However, in the case of Al^{3+}-mont-catalyzed aromatic alkylation of phenol with the aldehyde **1a** in the presence of bisphenols **3a**, the yield of 1-(hydroxyphenyl)butanes **2a** increased. These results suggested that alkylphenols **2** and bisphenols **3** might be produced competitively. The intermediary cations **I**, which were stabilized in the interlayer space of Al^{3+}-mont, might react electrophilically with phenol to produce **3** or might abstract a hydride[10] from bisphenols **3** or some other species to produce **2**.[11]



I

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References and Notes

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6 To phenol (2.50 g, 26.6 mmol) in a 20-cm^3 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 tentatively estimated by NH_3-TPD[1a]) at *ca.* 40 °C with a magnetic stirring. The mixture was heated to 100 °C during *ca.* 15 min and kept at the temperature for *ca.* 45 min. The octanal **1d** (100 mg, 0.78 mmol) was added dropwise to it and the mixture was stirred vigorously for 48 h. After it had been cooled, the catalyst was filtered and washed with diethyl ether (20 cm^3). Removal of the organic solvent including unreacted phenol from a mixture of the filtrate and the ether washings by distillation under reduced pressure and then removal of the remaining phenol by washing with dilute aqueous NaOH left a brown oil which was subjected to column chromatography (Wakogel C-300, eluents: hexane, hexane–ethyl acetate and ethyl acetate). The products were a colorless oil of 1-(hydroxyphenyl)octanes **2d** (hexane–ethyl acetate as eluents; 40.2 mg, 25% isolated yield, *o*- : *p*- = 8 : 92 determined by GLC) and a colorless oil of 1,1-bis(hydroxyphenyl)octanes **3d** [ethyl acetate as an eluent; 135.1 mg, 58% isolated yield; a mixture of three components of *ca.* 5 : 3 : 2 ratio in GLC; tentatively assigned by 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 **3** were similarly assigned.

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8 Under the reported conditions of Ref. 5 ($AlCl_3$ catalyst, 120 °C, 3 h), phenol reacted with **1f** and **1g** to give only the corresponding alkylphenols in 19% (*o*- : *p*- = 8 : 92) and 27% (*o*- : *p*- = 0 : 100), respectively, in our hands.

9 The alkylation also proceeded smoothly with anisole, sluggishly with toluene, but not with benzene and chlorobenzene. Details will be reported in a full account.

10 R. M. Roberts and A. A. Khalaf, in "*Friedel–Crafts Alkylation Chemistry*," Marcel Dekker, New York (1984), Ch. 8, pp 701 – 762.

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