

Rearrangement of Alkyl Phenyl Ethers to Alkylphenols in the Presence of Cation-exchanged Montmorillonite (M^{n+} -Mont)

Jun-ichi Tateiwa, Takahiro Nishimura, Hiroki Horiuchi and Sakae Uemura*

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

The rearrangement of alkyl phenyl ethers such as 4-phenoxybutan-2-one **1**, 1-phenoxybutane **2a**, 2-phenoxybutane **2b**, 2-methyl-2-phenoxypropane **2c** and phenoxy-cyclohexane **2d** have been investigated in the presence of cation-exchanged montmorillonite (M^{n+} -mont; $M^{n+} = Zr^{4+}$, Al^{3+} , Fe^{3+} and Zn^{2+}). The ether **1** rearranged to 4-(4-hydroxyphenyl)butan-2-one **3** (raspberry ketone), the odour source of raspberry, in 16–34% GLC yield, where Zn^{2+} -mont was the most effective catalyst. Similarly, other ethers **2a–d** rearranged to the corresponding alkylphenols in up to 75% isolated yield with good product selectivity, Al^{3+} -mont being the catalyst of choice. Al^{3+} -Mont was regenerated and reused in the rearrangement of **2b**, **2c** and **2d**.

We are currently interested in the catalytic use of cation-exchanged montmorillonite (M^{n+} -mont), a kind of modified natural clay, in organic synthesis under mild conditions.¹ M^{n+} -Mont has advantages such as ease of handling, noncorrosiveness, low cost, elimination of metal wastes such as aluminium (environmentally friendly catalyst²), regeneration and ready modification of acidity by cation exchange in the interlayer space.^{3,4} Although phenol-producing rearrangements such as the Fries rearrangement⁵ and the rearrangement of allyl phenyl ethers⁶ have been studied in the presence of clay catalysts, the rearrangement of alkyl phenyl ethers to produce alkylphenols has not. However, the AlX_3 -catalysed rearrangement of alkyl phenyl ethers to give alkylphenols is known, although since the latter were obtained only in low yields together with by-products,⁷ this reaction is of little use in synthesis.⁸

During our studies on the preparation of 4-(4-hydroxyphenyl)butan-2-one **3** by M^{n+} -mont-catalysed Friedel-Crafts alkylation of phenol with 4-hydroxybutan-2-one (γ -KB) or but-3-en-2-one (MVK),^{1a} we found that a facile rearrangement of 4-phenoxybutan-2-one **1** to the alkylphenol **3** occurs in the presence of M^{n+} -mont ($M^{n+} = Zr^{4+}$, Al^{3+} , Fe^{3+} and Zn^{2+}) under a variety of conditions. We also attempted to apply this rearrangement to non-functionalised-alkyl phenyl ethers such as 1-phenoxybutane **2a**, 2-phenoxybutane **2b**, 2-methyl-2-phenoxypropane **2c** and phenoxy-cyclohexane **2d** to obtain the corresponding alkylphenols. Some alkylphenols are useful for industrial and agricultural chemicals, that is, *o*-sec-butylphenol **5b** as a precursor of insecticides, acaricides and herbicides, *p*-*tert*-butylphenol **6c** as an antioxidant, the monomer of resins, the intermediate of emulsifiers and perfume and *o*-cyclohexylphenol **5d** as a precursor of pharmaceuticals and agrochemicals.⁹ The results are described in this report.

Results and Discussion

Rearrangement of 4-Phenoxybutan-2-one 1 to 4-(4-Hydroxyphenyl)butan-2-one 3.—During our studies on the Friedel-Crafts *C*-alkylation of phenol with 4-hydroxybutan-2-one (γ -KB) in the presence of M^{n+} -mont to produce compound **3**,^{1a} we found a convenient procedure for preparing compound **1**. Namely, when a small amount of pyridine was added to this alkylation system using Zr^{4+} -mont, phenol was *O*-alkylated selectively to give **1** in 43% isolated yield (49% GLC yield) *via* a Michael-type reaction. The reaction did not proceed in the absence of Zr^{4+} -mont. With Al^{3+} -mont in place of Zr^{4+} -mont, the reaction gave **1** in 26% GLC yield. On the other hand, but-3-

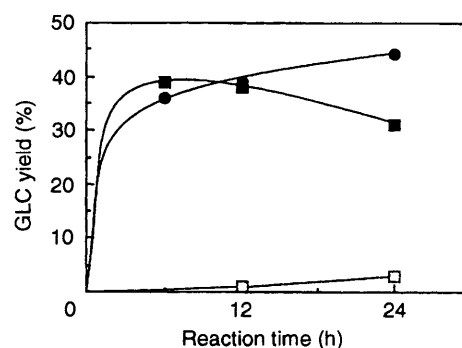


Fig. 1 Time course of Michael type reaction of phenol (2.67 g, 28.4 mmol) with 4-hydroxybutan-2-one (γ -KB, 500 mg, 5.67 mmol) to produce **3** in the presence of both Zr^{4+} -mont (500 mg, 0.367 mmol as acid sites) and pyridine (49 mg, 0.62 mmol) at 100 °C (■) and in the absence of Zr^{4+} -mont (□). Time course of the reaction of phenol (2.67 g, 28.4 mmol) with but-3-en-2-one (MVK, 397 mg, 5.67 mmol) in the presence of both Zr^{4+} -mont (500 mg, 0.367 mmol as acid sites) and pyridine (49 mg, 0.62 mmol) at 100 °C (●); almost the same curve was observed even in the absence of Zr^{4+} -mont.

en-2-one (MVK) showed reactivity similar to γ -KB to produce **1** even in the absence of Zr^{4+} - or Al^{3+} -mont (Fig. 1). Since the addition of phenol to MVK in the presence of pyridine is known,¹⁰ these results suggest that γ -KB was dehydrated first to MVK by M^{n+} -mont under the conditions employed and the resulting MVK reacted with phenol to produce **1**.

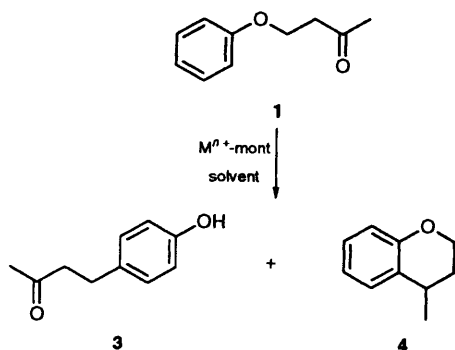
Compound **1** when heated with phenol in the presence of Zn^{2+} -mont at 100 °C for 48 h gave the alkylphenol **3** in 34% GLC yield with a complete consumption of **1** (Scheme 1; Table 1, run 4). A small amount of 4-methyl-3,4-dihydro-2H-1-benzopyran (4-methylchroman) **4** was obtained at the same time. The turnover number was estimated to be 5 based on the number of acid sites on Zn^{2+} -mont. Zn^{2+} -Mont was the most effective catalyst of the M^{n+} -monts examined, but it did not work well either below or above 100 °C (Table 1, runs 1–9). When either chlorobenzene or toluene was used as the solvent instead of phenol, only the decomposition of **1** to phenol occurred (Table 1, runs 11 and 12). Although the number of acid sites in the M^{n+} -mont determined by the temperature-programmed desorption of ammonia gas (NH_3 -TPD)^{1a} may not accurately represent the active acid sites (Lewis and Brønsted acid sites) available to this rearrangement, it provides a reference for M^{n+} -mont acidity.

In order to determine the thermodynamic stability of the

Table 1 Rearrangement of 4-phenoxybutan-2-one **1** in the presence of M^{n+} -mont^a

Run	M^{n+} -Mont (mmol) ^b	Solvent	Reaction temp. (°C)	GLC yield (%) ^c		Turnover number ^d
				3	4	
1	Zr ⁴⁺ -mont (0.367)	PhOH	100	24	3	2
2	Al ³⁺ -mont (0.266)	PhOH	100	16 (10) ^e	9 (8) ^e	2
3	Fe ³⁺ -mont (0.175)	PhOH	100	22	3	3
4	Zn ²⁺ -mont (0.186)	PhOH	100	34	3	5
5	H ⁺ -mont ^f	PhOH	100	Trace	0	—
6	Na ⁺ -mont (0) ^g	PhOH	100	Trace	0	—
7	Zn ²⁺ -mont	PhOH	25	Trace	0	0
8	Zn ²⁺ -mont	PhOH	50	Trace	0	0
9	Zn ²⁺ -mont	PhOH	150	14	2	2
10	Zn ²⁺ -mont (0.019) ^h	PhOH	100	5	Trace	6
11	Zn ²⁺ -mont (0.186)	PhCl	100	Trace	0	0
12	Zn ²⁺ -mont (0.186)	PhMe	100	Trace	0	0

^a **1** (400 mg, 2.44 mmol), M^{n+} -mont (500 mg), solvent (26.6 mmol) for 48 h. ^b The amount of acid sites. ^c Based on **1**. ^d Determined by the amount of acid sites on M^{n+} -mont. ^e Isolated yield. ^f K10, Aldrich Chemical Co., Inc. ^g Kunipia G, Kunimine Industries Co., Ltd. ^h Zn²⁺-mont, 50 mg.



isomers **1** and **3**, the heat of formation of each compound was calculated by the AM1 method.¹¹ Since the calculated heat of formation of **1** was 13.50 kcal mol⁻¹ higher than that of **3**, the rearrangement of **1** to **3** is predicted to be thermodynamically favourable.

Rearrangement of Alkyl Phenyl Ethers 2 to Alkylphenols 5 and 6.—Rearrangement of the butyl phenyl ethers **2a**, **2b** and **2c**, in place of **1**, was attempted in phenol as solvent (Scheme 2,

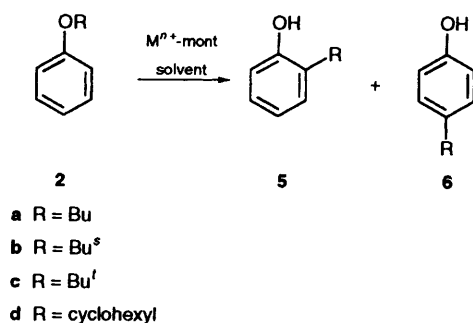


Table 2). Unlike **1**, **2a** failed to rearrange with Zn²⁺-mont as a catalyst, although it did so effectively over 48 h in the presence of Al³⁺-mont at 100 °C to produce compound **5b** and *p*-*sec*-butylphenol **6b**, both in 36% isolated yield (*ortho*:*para* = 50:50) (Table 2, run 2); no butylphenols **5a** and **6a** were produced and the reaction was incomplete after 24 h. Compound **2b** was more reactive than **2a** and rearranged within 1 h to **5b** and **6b** in 49 and 16% isolated yield (*ortho*:*para* = 75:25), respectively (Table 2, run 8). A facile rearrangement of

2c also occurred in the presence of Al³⁺-mont to produce compound **6c** selectively in 71% yield (Table 2, run 14). When the rearrangement of **2a** and **2b** was carried out in chlorobenzene as the solvent in place of phenol, the selectivity of the products improved (Table 2, runs 5 and 9) such that the product distribution of *ortho*/*para* changed from 50:50 to 66:34 and from 75:25 to 93:7 with **2a** and **2b**, respectively. Such a rearrangement also proceeded smoothly with **2c** and **2d** to give only a *para*-isomer **6c** and an *ortho*-rich mixture of **5d** and **6d** (**5d** > **6d**), respectively (Table 2, runs 15 and 20). In the rearrangement of **2d** (1h, 100 °C, PhCl) there was no evidence of (1-methylcyclopentyl)phenol formation although for the rearrangement of **2b** (48 h, PhCl) a little **6c** was formed besides the major products **5b** and **6b**. Even in the presence of a decreased amount (1/10th) of Al³⁺-mont, the rearrangement of **2b** and **2c** went to completion with only a slight decrease in product selectivity, but with an improvement in the turnover number (from 3–4 to 31–34; Table 2, runs 12 and 18). These reactions failed in the absence of M^{n+} -mont. Al³⁺-Mont was regenerated and reused for the rearrangement of **2b**, **2c** and **2d** in chlorobenzene as shown in runs 10, 11, 16, 17, 21 and 22 of Table 2. In the case of **2a**, however, the recovered Al³⁺-mont could not be reused, probably because of the deposition of some polymeric and tarry compounds on acid sites of the Al³⁺-mont during the longer reaction time (Table 2, run 6).

Rearrangement of **2b**, **2c** and **2d** in toluene as solvent with Al³⁺-mont as a catalyst at 100 °C for 1 h gave the corresponding alkyltoluenes as the major products in good yields (Table 2, runs 13, 19 and 23). From *sec*-alkyl phenyl ethers **2b** and **2d**, the corresponding alkylphenols were also obtained, although in lower yields, but with almost the same *ortho*/*para* ratio as that found with chlorobenzene as solvent. From *tert*-butyl phenyl ether **2c** much phenol was formed but no *tert*-butylphenols. Rearrangement of butyl phenyl ether **2a** in toluene for 48 h gave many by-products (*e.g.* alkyltoluenes and polymeric compounds) but only a small amount of the *sec*-butylphenols **5b** and **6b**.

AlCl₃ and AlBr₃ are known catalysts for the rearrangement of **2a** and **2b** to **5** and **6** (*ca.* 1–26% yield) at 0–5 °C either neat or in a solvent.^{7d,e} Attempted rearrangement of **2a**, **2b** and **2c** in the presence of varying quantities of anhydrous AlCl₃ (0.27–1.33 mmol) in place of Al³⁺-mont under our conditions (100 °C, 1–48 h) resulted in slow reactions and little of the expected butylphenols.

The heats of formation of **2a**, **2b**, **2c**, **5b**, **5c**, **6c** and *m*-*tert*-butylphenol are 10.47, 14.12, 19.68, 1.11, 7.20, 4.95 and 4.94 kcal mol⁻¹, respectively, compared to the heat of formation of **6b** as a standard (0.00 kcal mol⁻¹), all were calculated by AM1

Table 2 Rearrangement of alkyl phenyl ethers **2** in the presence of M^{n+} -mont^a

Run	Reactant	M^{n+} -Mont (mmol) ^b	Solvent	Time (h)	Product and isolated yield (%) ^c			Turnover number ^d
					5b	6b	5/6 ratio	
1	2a	Zr ⁴⁺ -mont (0.367)	PhOH	48	24	24	50/50	2
2	2a	Al ³⁺ -mont (0.266)	PhOH	48	36	36	50/50	4
3	2a	Fe ³⁺ -mont (0.175)	PhOH	48	0	0	—	0
4	2a	Zn ²⁺ -mont (0.186)	PhOH	48	0	0	—	0
5	2a	Al ³⁺ -mont (0.266) 1st	PhCl	48	29	15	66/34	3
6	2a	Al ³⁺ -mont (0.266) 2nd	PhCl	48	2	17	11/89	1
7	2a	Al ³⁺ -mont (0.027) ^e	PhCl	48	Trace	Trace	—	0
8	2b	Al ³⁺ -mont (0.266)	PhOH	1	49	16	75/25	3
9	2b	Al ³⁺ -mont (0.266) 1st	PhCl	1	53	4	93/7	3
10	2b	Al ³⁺ -mont (0.266) 2nd	PhCl	1	60	5	93/7	3
11	2b	Al ³⁺ -mont (0.266) 3rd	PhCl	1	63	6	91/9	3
12	2b	Al ³⁺ -mont (0.027) ^e	PhCl	1	61	9	88/12	34
13	2b	Al ³⁺ -mont (0.266)	PhMe	1	23	4 ^f	85/15	1
					5c	6c		
14	2c	Al ³⁺ -mont (0.266)	PhOH	1	0	71	0/100	4
15	2c	Al ³⁺ -mont (0.266) 1st	PhCl	1	0	75	0/100	4
16	2c	Al ³⁺ -mont (0.266) 2nd	PhCl	1	0	70	0/100	4
17	2c	Al ³⁺ -mont (0.266) 3rd	PhCl	1	0	65	0/100	4
18	2c	Al ³⁺ -mont (0.027) ^e	PhCl	1	4	55	7/93 ^g	31
19	2c	Al ³⁺ -mont (0.266)	PhMe	1	0	0 ^h	—	0
					5d	6d		
20	2d	Al ³⁺ -mont (0.266) 1st	PhCl	1	55	15	79/21	4
21	2d	Al ³⁺ -mont (0.266) 2nd	PhCl	1	53	9	85/15	3
22	2d	Al ³⁺ -mont (0.266) 3rd	PhCl	1	52	9	85/15	3
23	2d	Al ³⁺ -mont (0.266)	PhMe	1	25	5 ⁱ	83/17	2

^a **2** (1.33 mmol), M^{n+} -mont (500 mg), solvent (26.6 mmol) at 100 °C. ^b The amount of acid sites. ^c Based on **2**. ^d Determined by the amount of acid sites on M^{n+} -mont. ^e Al³⁺-mont, 50 mg. ^f *sec*-Butyltoluenes, 52% yield. ^g Determined by ¹H NMR. *m-tert*-Butylphenol, 4% yield. ^h *tert*-Butyltoluenes, 54% yield. ⁱ Cyclohexyltoluenes, 56% yield

method.¹¹ This result supports the rearrangement of butyl phenyl ethers **2a–c** to the thermodynamically more stable butylphenols **5b**, **5c**, **6b**, **6c** and *m-tert*-butylphenol. Similarly, the calculated heat of formation of **2d** was 15.4 and 14.3 kcal mol⁻¹ higher than that of **6d** and **5d**, respectively, such that a rearrangement of **2d** to **5d** and **6d** is predicted to be thermodynamically favourable.

Although the details of the reaction pathway are uncertain, the following overall path seems likely, being consistent with the mechanism proposed for the AlX₃-catalysed rearrangement.^{7c–e} Initially stable alkyl cations are formed by alkyl C–O bond fission as a result of interaction between oxygen and a Lewis acid site (aluminium); these may be stabilised by the negatively charged oxygens in the interlayer space of M^{n+} -mont. The cations attack aromatic carbons of phenol electrophilically to produce the corresponding alkylphenols. The experimental results such as the selective formation of *sec*-butylphenols **5b** and **6b** from butyl phenyl ether **2a**, the sole formation of *p-tert*-butylphenol **6c** from *tert*-butyl phenyl ether **2c** and the favourable formation of alkyltoluenes in toluene solvent show that the rearrangement mainly proceeds intermolecularly. In the *sec*-alkyl case, the path *via* intramolecular migration of an alkyl cation in the interlayer space might also be operative considering that *o*-alkylphenols **5b** and **5d** are the major products.

Conclusion.—The 3-oxobutyl phenyl ether **1** isomerised to the ketone **3** regioselectively in the presence of M^{n+} -mont ($M^{n+} = Zr^{4+}$, Al³⁺, Fe³⁺ and Zn²⁺) in 16–34% GLC yield. Similarly, non-functionalised alkyl phenyl ethers **2a–d** rearranged to the corresponding alkylphenols in the presence of

Al³⁺-mont in up to 75% isolated yield. The main reaction path is thought to be alkyl C–O bond fission to form a stable carbocation followed by its intermolecular attack on an aromatic carbon. In the case of *sec*-alkyl phenyl ethers, intramolecular migration of the cation might also be operative. The rearrangement of alkyl phenyl ethers in the presence of M^{n+} -mont has potential as a way of preparing alkylphenols in moderate to good yields; in this respect it is superior to AlX₃-catalysed rearrangement the yields for which are lower. Al³⁺-Mont may be regenerated and reusable in some cases.

Experimental

¹H NMR spectra were recorded on JEOL EX-400 (400 MHz) and JEOL GSX-270 (270 MHz) instruments for solutions in CDCl₃ with Me₄Si as an internal standard. ¹³C NMR spectra were obtained with JEOL EX-400 (100 MHz), JEOL GSX-270 (67.8 MHz) and JEOL FX-100 (25.0 MHz) instruments for solutions in CDCl₃ with Me₄Si as an internal standard. Coupling constants *J* are given in Hz. Mass spectra were measured on a Shimadzu QP-2000 mass spectrometer equipped with a Shimadzu GC-14A gas-liquid chromatography (25 m × 0.20 mm, 2.5 μm film thickness, Shimadzu fused silica capillary column HiCap CBP10-M25-025). The electron-impact method was used for ionisation and the ionising voltage was 70 eV for all compounds. GLC analyses were performed on a Hitachi 163 instrument (2 m × 3 mm stainless-steel column packed with 3% OV-17 on Chromosorb W and/or 25 m × 0.33 mm, 5.0 μm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionisation detectors and N₂ carrier gas with dibutyl phthalate as an internal

standard. Column chromatography on SiO₂ was performed with Wakogel C-200 and C-300 using hexane and hexane-ethyl acetate as eluents. 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.¹² Kunipia G, namely Na⁺-mont, was obtained from Kunimine Industries Co., Ltd. Mⁿ⁺-Mont (Mⁿ⁺ = Zr⁴⁺, Al³⁺, Fe³⁺ and Zn²⁺) was prepared by treatment of Na⁺-mont with the corresponding metal oxychloride or nitrate in aqueous acetone as described elsewhere.^{1a} Compound **2b** was prepared by following a slight modification of the reported method,^{7b} in which phenol was treated with 2-bromobutane in the presence of 50% aqueous NaOH at reflux temperature in one pot and identified by ¹H NMR¹³ and MS.¹⁴ Compound **2c** was prepared by the reported method and identified by ¹H NMR¹⁵ and MS.¹⁴ Compound **2d** was synthesised by following a slight modification of the reported method,¹⁶ in which phenol was treated with bromocyclohexane in the presence of 50% aqueous NaOH and toluene at reflux temperature in one pot and identified by ¹³C NMR¹⁷ and mass spectroscopy.¹⁴ Compound **4** is a known compound and identified by comparison of ¹H NMR spectra.¹⁸ Compounds **2a**, **3**, **5b**, **6b**, **5c**, **6c**, **5d**, **6d** and *m-tert*-butylphenol were commercially available. New spectral data of compounds **2b-d** are shown below.

4-Phenoxybutan-2-one 1.—Phenol (2.67 g, 28.4 mmol), Zr⁴⁺-mont (250 mg, 0.184 mmol as acid sites) and pyridine (49 mg, 0.62 mmol) were mixed at *ca.* 40 °C with a magnetic stirring. The temperature of the mixture was raised to 100 °C during *ca.* 30 min and the mixture was stirred for a further 15 min. 4-Hydroxybutan-2-one (γ -KB; 500 mg, 5.67 mmol) was then added dropwise to the mixture in 5 min at 100 °C and the mixture was stirred at that temperature for 12 h. After cooling, the catalyst was filtered off and washed with diethyl ether (20 cm³). A combined mixture of the filtrate and ether washings was washed with 10% aqueous NaOH (3 \times 20 cm³) in order to remove completely unchanged phenol. Evaporation of the solvent left a brown oil which was subjected to column chromatography [Wakogel C-200, eluent: hexane-ethyl acetate (95:5)]. Removal of the solvent by rotary evaporation left a colourless oil of 4-phenoxybutan-2-one **1** (399.1 mg, 2.43 mmol, 43% yield, GLC yield 49%). The identification of **1** has been reported previously.^{1a}

2-Phenoxybutane 2b. A colourless oil isolated by column chromatography; δ_c (100 MHz; CDCl₃) 9.8 (q), 19.3 (q), 29.2 (t), 74.9 (d), 115.9 (d), 120.4 (d), 129.5 (d) and 158.3 (s); *m/z* 150 (M⁺, 5%) and 94 (100).

2-Methyl-2-phenoxypropane 2c. A colourless oil isolated by column chromatography; δ_c (100 MHz; CDCl₃) 28.8 (q), 78.2 (s), 123.2 (d), 124.2 (d), 128.8 (d) and 155.3 (s); *m/z* 150 (M⁺, 1%) and 94 (100).

Phenoxy-cyclohexane 2d. A colourless oil isolated by distillation; b.p. 93.5/0.3 mmHg (lit.,¹⁶ 252–254 °C/744 mmHg; 1 mmHg = 133.32 Nm⁻²); δ_H (400 MHz; CDCl₃) 1.28–2.01 (10 H, m), 4.23 (1 H, tt, *J* 8.8, 3.9), 6.88–6.93 (1 H, m), 6.90 (2 H, d, *J* 8.3) and 7.25 (2 H, t, *J* 8.1); δ_c (100 MHz; CDCl₃) 23.8 (t), 25.6 (t), 31.9 (t), 75.4 (d), 116.1 (d), 120.5 (d), 129.4 (d) and 157.8 (s); *m/z* 176 (M⁺, 4%) and 94 (100).

Rearrangement of 4-Phenoxybutan-2-one 1 in Phenol in the Presence of Al³⁺-Mont to produce 4-(4-Hydroxyphenyl)butan-2-one 3 (Table 1, run 2).—To phenol (2.50 g, 26.6 mmol) was added Al³⁺-mont (500 mg, 0.266 mmol as acid sites) at *ca.* 40 °C with a magnetic stirring. The mixture was heated to 100 °C during *ca.* 30 min and stirred for 15 min. To the mixture was added 4-phenoxybutan-2-one **1** (400 mg, 2.44 mmol) dropwise

during 5 min at that temperature after which the mixture was stirred magnetically for 48 h. After cooling, the catalyst was filtered off and washed with diethyl ether (20 cm³). The combined filtrate and washings were treated with 10% aqueous NaOH (3 \times 20 cm³). After acidification of the alkaline extract with 17% aqueous HCl (25 cm³), the resulting solution was extracted with diethyl ether (4 \times 20 cm³). The ethereal extract was washed with brine, dried (MgSO₄), and subjected to rotary evaporation to leave a brown oil. This was subjected to column chromatography several times for purification [Wakogel C-200, eluents: hexane and then hexane-ethyl acetate (95:5 to 80:20)]. Evaporation of the chromatographic fractions left a pale yellow oil which was dissolved in diethyl ether-hexane (1:9) and the solution stored at room temperature to afford a colourless needle-like crystal of compound **3** (41.1 mg, 0.25 mmol, 10% yield, GLC yield 16%).

The mixture of the filtrate and ether washings left after alkaline extraction was washed with water (20 cm³), dried (MgSO₄) and evaporated to leave a brown oil which was subjected to flash column chromatography [Wakogel C-300, eluent: hexane]. Removal of the solvent left a colourless oil of 4-methylchroman **4** (30.0 mg, 0.20 mmol, 8% yield, GLC yield 9%); δ_c (100 MHz; CDCl₃) 22.2 (q), 28.5 (d), 30.3 (t), 63.9 (t), 116.7 (d), 120.2 (d), 127.2 (d), 127.6 (s), 128.7 (d) and 154.3 (s); *m/z* 148 (M⁺, 50%), 133 (100), 105 (44), 91 (28), 77 (24), 51 (24) and 39 (26). In other cases, the products were quantified by GLC analyses with dibutyl phthalate as an internal standard.

Rearrangement of Phenoxy-cyclohexane 2d in Toluene in the Presence of Al³⁺-Mont to produce the Cyclohexylphenols 5d and 6d and Cyclohexyltoluenes (Table 2, run 23).—To toluene (2.45 g, 26.6 mmol) was added Al³⁺-mont (500 mg, 0.266 mmol as acid sites) at room temperature with a magnetic stirring. Over *ca.* 30 min the stirred mixture was heated to 100 °C at which temperature it was kept for a further 15 min. To the mixture at the same temperature was added dropwise the phenoxy-cyclohexane **2d** (234 mg, 1.33 mmol) over 5 min; the mixture was then stirred magnetically for 1 h. After the mixture had cooled, the catalyst was filtered off and washed with diethyl ether (20 cm³). Evaporation of the filtrate and washings left a brown oil which was subjected to column chromatography [Wakogel C-300, eluent: hexane] to provide first cyclohexyltoluenes as a colourless oil (127.3 mg, 0.74 mmol, 56% yield). Successive column chromatography [eluent: hexane-ethyl acetate (98:2)] afforded compound **5d** (57.5 mg, 0.33 mmol, 25% yield) and **6d** (11.8 mg, 0.13 mmol, 5% yield) as a colourless oil. Compounds **5d** and **6d** were identified by comparison of their ¹H NMR, ¹³C NMR and mass spectra with those of authentic commercial samples.

Compounds **2** were similarly rearranged in phenol, chlorobenzene or toluene to give alkylphenols and alkyltoluenes on isolation by flash column chromatography [Wakogel C-300, eluents: hexane and hexane-ethyl acetate (98:2)]. Al³⁺-Mont was regenerated by washing with acetone (10 cm³) at room temperature for 24 h with a magnetic stirring, followed by filtration and then by drying at 120 °C for 24 h.

sec-Butyltoluenes. A colourless oil isolated by column chromatography (hexane as eluent) and identified as a mixture of three isomers by GLC. Each of isomers showed a similar mass spectrum; *m/z* 148 (M⁺, 6%), 119 (100) and 91 (21) for major isomer (Found: C, 89.3; H, 10.8. Calc. for C₁₁H₁₆: C, 89.12; H, 10.88%).

tert-Butyltoluenes. A colourless oil isolated by column chromatography (hexane as eluent) and identified as a mixture of two isomers by GLC. Each of isomers showed similar mass spectrum; *m/z* 148 (M⁺, 27%), 133 (100), 105 (56), 93 (21) and 41 (40) for major isomer (Found: C, 89.3; H, 10.9. Calc. for C₁₁H₁₆: C, 89.12; H, 10.88%).

Cyclohexyltoluenes. A colourless oil isolated by column chromatography (hexane as eluent) and identified as a mixture of two isomers by GLC. Each of isomers showed a similar mass spectrum; m/z 174 (M^+ , 53%), 131 (100), 118 (60), 105 (57) and 91 (44) for major isomer (Found: C, 89.4; H, 10.5. Calc. for $C_{13}H_{18}$: C, 89.59; H, 10.41%).

Acknowledgements

We thank Professor Hiroshi Fujimoto, Mr. Yasuo Oishi and Mr. Tomohiro Suzuki of the Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, for AMI calculations. We also thank Kunimine Industries Co., Ltd. for the gift of Kunipia G.

References

- (a) J. Tateiwa, H. Horiuchi, K. Hashimoto, T. Yamauchi and S. Uemura, *J. Org. Chem.*, 1994, **59**, 5901; (b) J. Tateiwa, H. Horiuchi and S. Uemura, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2883.
- J. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow and P. Landon, *J. Chem. Soc., Chem. Commun.*, 1989, 1353; S. J. Barlow, J. H. Clark, M. R. Darby, A. P. Kybett, P. Landon and K. Martin, *J. Chem. Res.*, 1991, (S), 74.
- For recent reviews on the reactions in the presence of clay, see for example: M. Balogh and P. Laszlo, *Organic Chemistry Using Clays*, Springer-Verlag, New York, 1993; F. J. A. Kellendonk, J. J. L. Heinerman, R. A. van Santen, A. McKillop, D. W. Clissold, T. J. Pinnavaia, A. Foucaud and J. M. Adams, *Preparative Chemistry Using Supported Reagents*, ed. P. Laszlo, Academic Press, New York, 1987, part 8, pp. 453–528.
- Technical Information Bulletin AL-143, Aldrich Chemical Co., Inc., 1987.
- T. Fujita, M. Ishiguro, K. Takahata and K. Saeki, *Jap P* 85 252 444/1985 (*Chem. Abstr.*, 1986, **104**, 168144q); K. Pitchumani and A. Pandian, *J. Chem. Soc., Chem. Commun.*, 1990, 1613.
- W. G. Dauben, J. M. Cogen and V. Behar, *Tetrahedron Lett.*, 1990, **31**, 3241.
- (a) C. Hartmann and L. Gattermann, *Chem. Ber.*, 1892, **25**, 3531; (b) M. M. Sprung and E. S. Wallis, *J. Am. Chem. Soc.*, 1934, **56**, 1715; (c) P. A. Spaninger and J. L. von Rosenberg, *J. Chem. Soc., Chem. Commun.*, 1970, 795; (d) *J. Am. Chem. Soc.*, 1972, **94**, 1970; (e) 1972, **94**, 1973 and other references cited therein.
- For example, J. March, *Advanced Organic Chemistry*, 4th edn., Wiley, New York, 1992, ch. 11, pp. 556–557.
- H. Fiege and H.-W. Voges, *Ullmann's Encyclopedia of Industrial Chemistry*, 5th edn., ed. B. Elvers, S. Hawkins and G. Schulz, VCH, Weinheim, 1991, vol. A19, pp. 313–342.
- N. Yamashita, H. Inoue and T. Maeshima, *J. Polym. Sci.*, 1979, **17**, 2739.
- M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
- D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon Press, Oxford, 1980.
- J. Bergman, P.-O. Norrby and P. Sand, *Tetrahedron*, 1990, **46**, 6113.
- F. W. McLafferty and D. B. Stauffer, *The Wiley/NBS Registry of Mass Spectral Data*, Wiley, New York, 1989.
- H. Masada and Y. Oishi, *Chem. Lett.*, 1978, 57.
- B. W. Tronow and L. W. Ladigina, *Chem. Ber.*, 1929, **62**, 2844.
- W. Bremser, L. Ernst, B. Franke, R. Gerhards and A. Hardt, *Carbon-13 NMR Spectral Data*, Springer-Verlag, New York, 1979.
- M. P. Doyle, J. L. Whitefleet and R. J. Bosch, *J. Org. Chem.*, 1979, **44**, 2923.

Paper 4/04886E

Received 9th August 1994

Accepted 1st September 1994