Studies on Selective Preparation of Aromatic Compounds; 18[1]. A New Preparative Method for Aryl 4-Hydroxyphenyl Ethers

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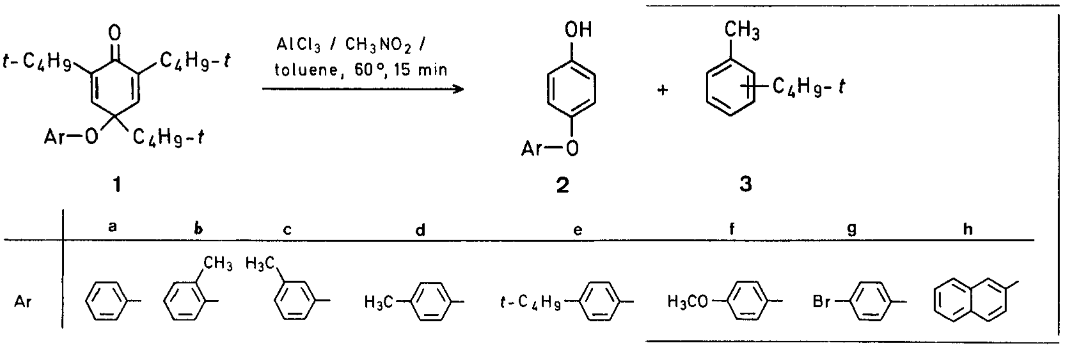
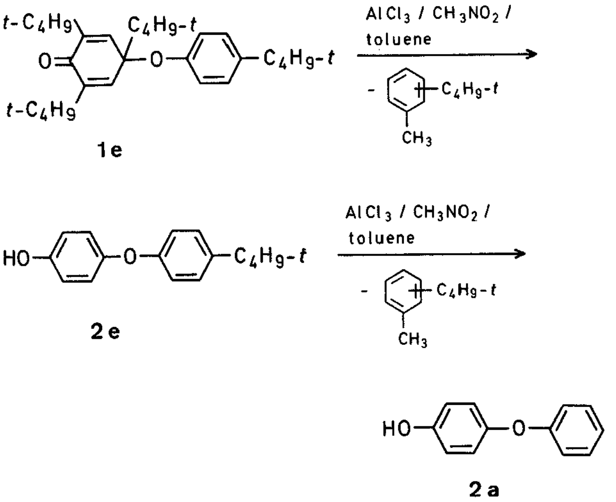
It has been previously reported that[2-6] the *t*-butyl group of some phenolic compounds could be transalkylated to an aromatic solvent such as benzene or toluene in the presence of a Lewis acid such as aluminium chloride/nitromethane or titanium(IV) chloride. It has been also found that 4-*t*-butyl-2,4,6-trichlorocyclohexa-2,5-dien-1-one[7] as well as 2,6-di-*t*-butyl-*p*-cresol[8,9,10] could be used as a *t*-butylating agent for aromatic compounds under the influence of a Lewis acid such as aluminium chloride or aluminium chloride/nitromethane.

The above results suggest that the aluminium chloride/nitromethane-catalyzed trans-*t*-butylation of 4-aryloxy-2,4,6-tris-[*t*-butyl]cyclohexa-2,5-dien-1-ones **1**, which can easily be prepared according to the method reported by Müller et al.[11] might afford the corresponding aryl 4-hydroxyphenyl ethers **2**.



The results of the aluminium chloride/nitromethane-catalyzed transalkylation of **1** in toluene are summarized in Table 1. As is shown in Table 1, the expected **2e** was not obtained in the transalkylation of **1e**, instead **2a**, which might be formed by further transalkylation of **2e**, was formed in 68% yield. Based on the above result it can be concluded that, as **1a** is an unstable liquid compound, **1e** may be a more suitable starting compound than **1a** for the preparation of **2a**.



The starting compounds **1** were prepared according to Müller's method and the results are summarized in Table 2.

4-Bromophenyl 4-Hydroxyphenyl Ether (2g); Typical Procedure: To a solution of **1g** (4.1 g, 9 mmol) in toluene (143 ml) is added at 60° a solution of aluminium chloride (3.6 g, 27 mmol) in nitromethane (6 ml). After the reaction mixture has been stirred at

Table 1. Preparation of Aryl 4-Hydroxyphenyl Ethers **2** by the Aluminium Chloride/Nitromethane-Catalyzed Transalkylation[a] of 4-Aryloxy-2,4,6-tris[*t*-butyl]cyclohexa-2,5-dien-1-ones **1**

Product	Yield[b] [%]	m.p. (solvent) (Lit. m.p.)	Molecular formula[c]	I.R. (KBr) ν_{max} [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]
2a	47 (68)[d]	83–85° (60–80° PE) (84–85°)[12]	$C_{12}H_{10}O_2$ (186.2)	3520–3080	5.91 (s, 1 H); 6.7–7.4 (m, 9 H)
2b	31	39–40° (60–80° PE)	$C_{13}H_{12}O_2$ (200.2)	3640–3080	2.30 (s, 3 H); 4.91 (s, 1 H); 6.75–7.5 (m, 8 H)
2c	71	oil[e]	$C_{13}H_{12}O_2$ (200.2)	3680–3080[f]	2.18 (s, 3 H); 6.6–7.2 (m, 8 H); 7.41 (s, 1 H)
2d	79	76.5–77.5° (60–80° PE)	$C_{13}H_{12}O_2$ (200.2)	3600–3120	2.28 (s, 3 H); 5.05 (s, 1 H); 6.5–7.3 (m, 8 H)
2f	57	91–91.5° (hexane)	$C_{13}H_{12}O_3$ (216.2)	3600–3120	3.76 (s, 3 H); 5.75 (s, 1 H); 6.75–7.10 (m, 8 H)
2g	83	86–87° (hexane) (88°)[13]	$C_{12}H_9BrO_2$ (265.1)	3640–3080	3.50 (s, 1 H); 6.7–7.5 (m, 8 H)
2h	84	87–88° (hexane)	$C_{10}H_{12}O_2$ (164.2)	3680–3080	4.95 (s, 1 H); 6.75–7.9 (m, 11 H)

[a] Reaction at 60° for 15 min; molar ratio of toluene: $AlCl_3$: **1** = 150:3:1.

[b] Formation of *t*-butyltoluenes **3** confirmed by G.L.C. (Yanagimoto Gas Chromatograph G8 YR-101; column 30% high vacuum silicon grease, 2 m, carrier gas, helium 50 ml/min, rate of increase of column temperature 12°/min); **3** formed mainly as *p*-isomer with 2–3% of *m*-isomer.

[c] All products gave satisfactory microanalyses (C ±0.26%, H ±0.07%).

[d] Yield of **2a** starting from **1e**, see text.

[e] Benzoate formed as colorless needles, m.p. 59–60° (C_2H_5OH).

[f] Neat between NaCl plates.

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Table 2. Preparation of 4-Aryloxy-2,4,6-tris[*t*-butyl]cyclohexa-2,5-dien-1-ones **1a–h**

Product	Yield [%]	m.p. (solvent)	Lit. m.p.	Molecular formula[a]	I.R. (KBr) ν_{max} [cm^{-1}]
1a	83	oil	oil[14]	—	—
1b	73	157–158° (dec.) (CH_3OH)	—	$C_{25}H_{36}O_2$ (368.6)	1640, 1660
1c	68	31–32° (CH_3OH)	—	$C_{25}H_{36}O_2$ (368.6)	1640, 1660
1d	77	71–72° (CH_3OH)	—	$C_{25}H_{36}O_2$ (368.6)	1640, 1660
1e	82	91.5–92.5° (CH_3OH)	91–92°[11]	$C_{28}H_{42}O_2$ (410.6)	1640, 1655
1f	71	78–79° (ether/CH_3OH)	77–78°[14]	$C_{25}H_{36}O_3$ (368.6)	1630, 1650
1g	80	102–103°	—	$C_{24}H_{33}BrO_2$ (433.4)	1635, 1660
1h	74	76–77°	75–76°[11]	$C_{28}H_{36}O_2$ (404.6)	1630, 1660

[a] All products gave satisfactory microanalyses (C ±0.32%, H ±0.29%).

60° for 15 min, it is quenched with ice/water, and extracted with ether. The ether solution is extracted with 10% sodium hydroxide solution. The alkaline solution is acidified with 10% hydrochloric acid and extracted with ether. The ether solution is dried with sodium sulfate and evaporated in vacuo to afford **2g** as colorless plates; yield: 2.08 g (83%); m.p. 86–87° (hexane).

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