

Improved Procedure for Preparation of *t*-Alkyl Aryl Ethers

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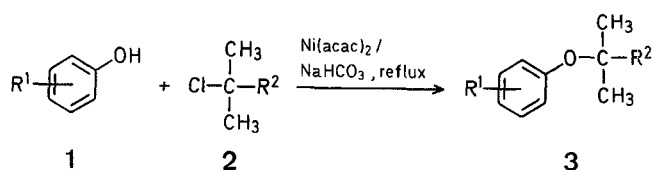
Methods so far reported in the literature for the preparation of *t*-alkyl aryl ethers **3** are scarce and somewhat sophisticated¹⁻⁷. The main drawback for the synthesis of these com-

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pounds arises from the occurrence of side reactions, either elimination reactions of the starting *t*-alkyl halide in basic media or rearrangements of the final product to *C*-alkylated phenols under acid conditions⁸. Recently, a synthesis of ethers from alcohols and alkyl halides in the presence of nickel bis[acetylacetonate] as catalyst has been described⁹. However, when this method was applied to phenols it failed to give the expected alkyl aryl ethers affording only rearranged products instead.

In the present communication, we report a convenient modification of the above procedure for the synthesis of *t*-alkyl aryl ethers **3** by using nickel bis[acetylacetonate] as catalyst and sodium hydrogen carbonate as hydrogen chloride acceptor. When a solution of a phenol **1** in a *t*-alkyl chloride **2** was refluxed in the presence of an excess of sodium hydrogen carbonate and a catalytic amount of nickel bis[acetylacetonate] the corresponding *t*-alkyl aryl ethers **3** were obtained in the yields summarized in the Table.



to 82% after performing three successive additions, whereas by carrying out the reaction in a single operation using a triple amount of catalyst, sodium hydrogen carbonate, and **2**, only 55% of **1a** was converted into the corresponding **3a**. Replacement of the above catalyst by other acetylacetonates (Cr, Co, VO) failed to improve the results of this reaction.

t-Butyl Phenyl Ether (**3a**); Typical Procedure:

A mixture of phenol (**1a**; 9.4 g, 0.1 mol), *t*-butyl chloride (**2**, R² = CH₃; 30 ml, 0.27 mol), nickel acetylacetonate (0.13 g, 0.5 mmol; previously dehydrated by refluxing for 8 h in a Dean-Stark apparatus with toluene) and sodium hydrogen carbonate (17 g, 0.2 mol) is stirred and refluxed at 60°C for 24 h. After this time most of the unreacted **2** has been eliminated as isobutylene. Diethyl ether (50 ml) is added to the residue, the solid is removed by filtration and washed twice with diethyl ether (2 × 10 ml). Then the remaining solid is dissolved in the minimum amount of water and this aqueous solution is extracted with diethyl ether (3 × 10 ml). The combined organic phases are repeatedly extracted with 5 normal aqueous sodium hydroxide solution (3 × 20 ml), dried with magnesium sulphate, and evaporated to dryness. The residue is distilled at reduced pressure to give **3a**; yield: 4.8 g (32%); b.p. 68–70°C/10 torr (Ref.¹, 70–71°C/11 torr). By acidification of the aqueous layer and extraction with diethyl ether the unreacted phenol is recovered (5.2 g; 55%).

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Table. *t*-Alkyl Aryl Ethers **3** prepared

Product No.	R ¹	R ²	Yield [%]	Conversion [%]	Ratio of C-/O-products	b.p. [°C]/torr		¹ H-N.M.R. (CCl ₄) δ [ppm]	Purity [%] ^a
						found	reported		
3a	H	CH ₃	32	45	0	68–70°/11	70–71°/11 ¹	1.28 (s, 9H); 6.7–7.4 (m, 5H)	99
3b	H	C ₂ H ₅	32	46	0	84–86°/10	104–105°/28 ⁵	1.00 (t, 3H); 1.23 (s, 6H); 1.68 (q, 2H); 6.7–7.4 (m, 5H)	99
3c	2-H ₃ CO	CH ₃	0	—	—	—	—	—	—
3d	3-H ₃ CO	CH ₃	22	52	0	106–108°/10	106°/10 ⁴	1.30 (s, 9H); 3.70 (s, 3H); 6.3–7.2 (m, 4H)	90
3e	4-H ₃ CO	CH ₃	32	48	0	108–110°/10	108–109°/9 ⁴	1.25 (s, 9H); 3.65 (s, 3H); 6.70, 6.85 (AB q, J=9 Hz, 4H)	99
3f	2-H ₃ C	CH ₃	15	37	1.25	75–76°/10	73°/9 ⁴	1.38 (s, 9H); 2.20 (s, 3H); 6.7–7.2 (m, 4H)	90
3g	3-H ₃ C	CH ₃	22	34	0	77–78°/10	85–86°/11 ⁴	1.30 (s, 9H); 2.30 (s, 3H); 6.7–7.2 (m, 4H)	98
3h	4-H ₃ C	CH ₃	35	43	0	80–81°/10	79–81°/10 ⁴	1.26 (s, 9H); 2.25 (s, 3H); 6.73, 6.91 (AB q, J=9 Hz, 4H)	99
3i	4-O ₂ N	CH ₃	0	—	—	—	—	—	—
3j	2-Cl	CH ₃	6	17	0.85	98–101°/10	— ^b	1.37 (s, 9H); 6.8–7.4 (m, 4H)	99
3k	3-F	CH ₃	8	38	0	62–65°/10	61°/9 ⁴	1.33 (s, 9H); 6.4–7.3 (m, 4H)	90
3l	4-Cl	CH ₃	17	25	0	102–104°/10	84–85°/9 ¹⁰	1.23 (s, 9H); 6.75, 7.10 (AB q, J=9 Hz, 4H)	96

^a By G.L.C. analysis (conditions: OV-101, 3% on chromosorb W; 2 m × 1/8 in column, 70°C (for **3a, b**) or 130°C.

^b C₁₀H₁₃ClO calc. C 65.04 H 7.10 Cl 19.20
(184.7) found 64.81 7.22 19.17

As shown from these results, the procedure failed in the case of phenols bearing strong electron-withdrawing substituents (**1i**). On the other hand, *ortho*-substituted phenols (**1c, 1f, 1j**) reacted rather sluggishly and variable amounts of rearranged products were found.

Apparently, the catalyst activity is strongly influenced by the presence of the water formed during the reaction. This fact could account for the moderate conversion values obtained, since we have observed that the overall conversion can be considerably increased by filtration and addition to the filtrate of new catalyst, sodium hydrogen carbonate, and *t*-alkyl chloride. Thus, the conversion value for **1a** was increased up

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