A Convenient Synthesis of Ethers from Alcohols and Alkyl Halides Catalysed by Bis[acetylacetonato]nickel

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Although there have been many reports on the ether linkage formation, little is known on their "direct" derivation from hydroxy compounds and halides[1]. In this communication, we wish to report a facile synthesis of ethers using bis[acetylacetonato]nickel which was found to be an efficient catalyst for the synthesis of ethers from alcohols and halides with the generation of hydrogen halides.

$$\underset{\mathbf{1}}{R^1-OH} + \underset{\mathbf{2}}{R^2-Hal} \xrightarrow[-HHal]{Ni(acac)_2} \underset{\mathbf{3}}{R^1-O-R^2}$$

When an equimolar mixture of an alcohol **1** and a halide **2** is heated under reflux in the presence of a catalytic amount of the nickel complex, evolution of a hydrogen halide occurs immediately and high yield of the corresponding ether **3** is obtained by distillation. Representative results are listed in the Table. This reaction can be conducted in an open vessel, the materials and catalyst can be used as obtained from the commercial source without further purification.

The high yields of the products and the facility of the procedure make this method attractive for the syntheses of ethers. By this method, however, phenol did not give the corresponding ether; the *ortho*-alkylated compound was obtained exclusively instead (Reaction 4).

Preparation of Benzyl *n*-Octyl Ether: Typical Procedure:
Benzyl chloride (40 mmol), *n*-octanol (40 mmol), and bis[acetylacetonato]nickel (1 mmol) are heated under reflux (190°) for 3 h. After filtration of the reaction mixture, fractional distillation of the filtrate gives benzyl *n*-octyl ether; yield: 7.5 g (85%); b.p. 90–91°/0.05 torr.

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[1] I. T. Harrison, S. Harrison, *Compendium of Organic Synthetic Methods*, Vol. 1, p. 309 (1971); Vol. 2, p. 127 (1974), Wiley-Interscience, New York.

[2] *Handbook of Chemistry and Physics*, 52 edn, Chemical Rubber Co., Cleveland, Ohio, 1972.

Table. Preparation of Ethers **3**

Entry	Alcohol **1** R^1-OH	Halide **2** R^2-Hal	Reaction temperature	Yield [%] of **3**	b.p./torr	Molecular formula[a]	Lit. b.p./torr
1	$C_6H_5-CH_2-OH$	$C_6H_5-CH_2-Cl$	210°	90	94–95°/0.3	$C_{14}H_{14}O$ (198.3)	160°/11[2]
2	n-$C_6H_{13}-OH$	$C_6H_5-CH_2-Cl$	180°	81	79°/0.6	$C_{13}H_{20}O$ (192.3)	—
3	n-$C_8H_{17}-OH$	$C_6H_5-CH_2-Cl$	190°	85	90–91°/0.05	$C_{15}H_{24}O$ (220.3)	—
4	C_6H_5-OH	$C_6H_5-CH_2-Cl$	180°	80[b]	102–102.5°/0.4	$C_{13}H_{12}O$ (184.2)	171°/13
5	n-$C_8H_{17}-OH$	n-$C_8H_{17}-Br$	190°	78	89–90°/0.5	$C_{16}H_{34}O$ (242.4)	286–287°/760[2]
6	$C_6H_5-CH_2-OH$	4-$H_3C-C_6H_4-CH_2-Cl$	210°	65	100°/0.2	$C_{15}H_{16}O$ (212.3)	110°/0.3
7	$C_6H_5-CH_2-OH$	n-$C_8H_{17}-Br$	210°	79	91°/0.05	$C_{15}H_{24}O$ (220.3)	—

[a] All products gave satisfactory microanalyses (C ±0.38%, H ±0.26%). [b] Product is 2-benzylphenol.