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# One-Pot Etherification of Ketones and Aldehydes with Organic Halides Using Sodium Hydride as a Reductant

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**Abstract:** One-pot etherification reaction of aromatic and some aliphatic carbonyl compounds with organic halides in the presence of sodium hydride as a reducing reagent proceeded smoothly in dioxane, a polar solvent with higher boiling point, to provide desired ethers in moderate to high yields.

Keywords: Aldehyde, etherification, ketone, one pot, sodium hydride

Ether functionalities, especially unsymmetrical ones, have had many useful applications in various chemical intermediates in the pharmaceutical, agricultural, and fragrance industries, for example. One of the common preparation methods of these ethers is the so-called Williamson reaction, which features the reaction between alkoxides (sodium, lithium, potassium, etc.) and alkyl halides. The normal sequence is to prepare the alkoxide from the corresponding alcohol and subsequently react it with alkyl halide via nucleophilic substitution.<sup>[1]</sup> The unsymmetrical ethers also can be prepared via reductive etherification of carbonyl compounds with a reducing reagent, such as decaborane<sup>[2]</sup> and triethylsilane.<sup>[3]</sup> The employment of triethylsilane needs the combination of a Lewis acid, such as trityl perchlorate,<sup>[3a]</sup> trimethylsilyl iodide,<sup>[3b,c]</sup> trimethylsilyl triflate,<sup>[3d]</sup>

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bismuth bromide,<sup>[3e]</sup> copper triflate,<sup>[3f]</sup> and tris(pentafluorophenyl)borane.<sup>[3g]</sup> Recently, Iwanami and coworkers reported that the reductive etherification of aldehydes and ketones proceeds with triethylsilane and alkoxytrimethylsilane in the presence of iron(III) chloride as a catalyst.<sup>[4]</sup>

During the course of our research on the preparation of unsymmetrical ethers, we found that NaH, which is usually used as a base in organic synthesis, can be utilized as a reductive hydride source for the reduction of ketones and aldehydes to offer sodium alkoxides, which could react smoothly with alkyl halide in a one-pot fashion to directly provide unsymmetrical ethers. This procedure will greatly simplify the existing protocol for reductive etherification, and we feel it could find general use among chemists. Herein we report our findings.

Initially, we studied the reductive etherification using various types of metal hydride in different solvents. The results are summarized in Table 1. Reaction between benzophenone (1a) and benzyl chloride was chosen as a model for screening purposes. As expected, the use of LiAlH<sub>4</sub> reduced benzophenone nicely but failed in the alkylation and provided the corresponding alcohol 3 in quantitative yield (entry 1). During the study, we observed complete decomposition of benzyl chloride by LiAlH<sub>4</sub>. NaBH<sub>4</sub> only provided the desired ether (2a) in minimum yield

	Ph Ph + 1a	BnCl reflux, 6 h	$\rightarrow \begin{array}{c} OBn \\ Ph \\ Ph \\ 2a \end{array} + $	Ph Ph 3
Entry	Reductant	Solvent	Yield of $2a (\%)^b$	Yield of $3 (\%)^b$
1	LiAlH <sub>4</sub>	THF	0	94
2	NaBH <sub>4</sub>	THF	4	86
3	CaH <sub>2</sub>	THF	0	0
4	NaH	THF	Trace <sup>c</sup>	Trace <sup>c</sup>
5	NaBH <sub>4</sub>	DME	4	87
6	$CaH_2$	DME	0	0
7	NaH	DME	87	0
8	$CaH_2$	Dioxane	0	0
9	NaH	Dioxane	92	0
10	NaH	Toluene	56	14

Table 1. Screening of reductant and solvent<sup>a</sup>

<sup>*a*</sup>Reaction conditions: benzophenone (1.0 mmol), benzyl chloride (1.3 mmol), reductant (1.3 mmol), and solvent (3 mL); reflux; 6 h.

<sup>b</sup>Isolated yields.

<sup>c</sup>Detected by GC.

(4%, entries 2 and 5) using either tetrahydrafuran (THF) or 1,2-dimethoxyethane (DME) as the solvent. The use of  $CaH_2^{[5]}$  resulted in no reaction (entries 3, 6, and 8). When NaH was first studied and THF was used as a reaction solvent, only trace amounts of **2a** and **3** were observed (entry 4). However, when DME and dioxane, polar solvents with higher boiling points than THF, were used as reaction solvents to substitute THF, the desired ether **2a** was formed in high yield (87% and 92% respectively, entries 7 and 9). When using toluene, moderate yield (56%) of **2a** was obtained along with **3** in 14% yield (entry 10).

Then we examined the general scope of the reductive etherification with various carbonyl substrates and organic halides. We are pleased to find that the protocol is successful in many ketones and aldehydes as long as they lack enolizable  $\alpha$ -protons. Our results are summarized in Table 2. Reductive etherification of dibenzylideneacetone (1b) with benzyl chloride provided the desired ether product 2b in 42% yield (entry 2). Carbonyl compounds that have enolizable  $\alpha$ -protons such as cyclohexanone (1c) and acetophenone (1d) did not work in this reductive etherification reaction (entries 3 and 4). In these cases, sodium hydride will simply act as a strong base and abstracts the acidic proton in the carbonyl substrates. The acid-base reaction proceeded much faster than the desired reduction of carbonyl group; thus, the reductive ether formation did not happen. The evidence becomes more clear in the studies of camphor (1e), which also has enolizable  $\alpha$ -protons. The three major products (2e, 4e, and 5e) isolated and identified from the reaction all related to the enolated intermediate, and none of the reductive product was observed (entry 5). From this study, we clearly see that this protocol should only be used in carbonyl substrates lacking enolizable  $\alpha$ -protons. In the example of 2-admantanone (1f), which contains unenolizable  $\alpha$ -proton because of the rigidity of its framework, the reductive etherification worked well to provide desired ether product in moderate to high yields (entries 6–13). This observation and hypothesis was further supported by the reaction shown in Scheme 1. When 1f reacted with NaH and was subsequently quenched with water, the reduction product (alcohol) was obtained in 92% yield. The etherification did not occur between 2-admantanone and 1-bromo-2-methylpropane (entry 14), because 1-bromo-2-methylpropane decomposes rapidly in the hot solution of strong base. We also found this protocol worked well on aldehyde substrates (entries 15–20).



Scheme 1. The evidence for supporting the hypothetic mechanism.

## **One-Pot Etherification**

Entry	Substrate		Organic halide	Product	Yield (%) <sup>b</sup>
1	Ph Ph	(1a)	BnCl	Ph $Ph$ $Ph$ $(2a)$	92
2	Ph (1b)	^Ph	BnCl	Ph $(2b)$ $Ph$ $Ph$	42
3	0=	(1c)	BnCl	Complex mixture	—
4	Ph Me	(1d)	BnCl	Complex mixture	—
5 <sup><i>c</i></sup>	× po	(1e)	BnCl	$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$	90
6	₽ <sup>0</sup>	( <b>1f</b> )	BnCl	O <sub>Bn</sub> (2f)	90
7	( <b>1f</b> )		Cl	(2g) Cl	87
8	( <b>1f</b> )		H <sub>3</sub> CO OCH	OCH <sub>3</sub> OCH <sub>3</sub> OCH <sub>3</sub> OCH <sub>3</sub>	87

**Table 2.** Etherification of ketones and aldehydes (1) with organic halides using sodium hydride as a reductant<sup>a</sup>

(Continued)

Entry	Substrate	Organic halide	Product	Yield (%) <sup>b</sup>
9	(1f)	CI N		51
10 <sup>d</sup>	(1 <b>f</b> )	Br	(2j)	70
11	(1 <b>f</b> )	Me-I	0. <sub>Me</sub> (2k)	87
12	(1 <b>f</b> )	Et-Br	O <sub>Et</sub> (21)	65
13	(1 <b>f</b> )	<i>n</i> -Bu–Br	<sup>O</sup> ·Bu· <i>n</i> (2m)	42
14	( <b>1f</b> )	Br	(2n)	0
15	PhCHO (1g)	BnCl	Bn <sup>-O</sup> -Bn (20)	77
16	Cl CHO (1h)	BnCl	Cl O <sup>-Bn</sup> (2p)	86
17	O <sub>2</sub> N (1i)	BnCl	$O_{2N}$ $O'^{Bn}$ $(2q)$	26
18	OMe CHO OMe (1j)	BnCl	OMe OMe (2r)	72

Table 2. Continued

(Continued)

Table	2.	Continue	d
	_	0011011000	~

Entry	Substrate	Organic halide	Product	Yield (%) <sup>t</sup>
19	MeO (1k)	CI	MeO (2s) Cl	63
20	Ph CHO (11)	<i>■ B</i> r	Ph(2t)	75

<sup>*a*</sup>All reactions were carried out under nitrogen at reflux for 6 h using ketone or aldehyde (1.0 mmol), organic halide (1.3 mmol), sodium hydride (1.3 mmol), and dioxane (3 mL), unless otherwise noted. The reaction progress was monitored by TLC.

<sup>b</sup>Isoleted yields.

<sup>c</sup>1.5 mmol of benzyl chloride and sodium hydride, respectively, were used. The ratio of 2e:4e:5e is 19:8:3.

<sup>*d*</sup>After the mixture of **1f** and NaH was treated at reflux for 6 h, which was cooled to  $50^{\circ}$ C, methyl iodide was added to the mixture. The reaction mixture obtained was stirred at  $50^{\circ}$ C for an additional 2 h.

Overall, we reported in this article a useful protocol for reductive etherification in one-pot fashion. The protocol uses inexpensive and readily available sodium hydride as reductant. From our extended study, we found this protocol should be useful in many different types of carbonyl compounds and alkyl halides. It should find general use in organic synthesis.

### **EXPERIMENTAL**

All solvents were used with further purification. All products were purified by flash-column chromatography using silica gel 60 (200–300 mesh). <sup>1</sup>H NMR spectra were obtained from either a Varian Inova 400 or Bruker Avance 400 spectrometer with tetramethylsilane (TMS) as an internal standard. The symbols s, d, t, q, and m stand for singlet, doublet, triplet, quartet, and multiplet respectively. <sup>13</sup>C NMR spectra were recorded at 100 MHz on the Bruker Avance 400 spectrometer. High-resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometer (Micromass, England) equipped with Z-spray ionization source. Elemental analysis were performed on the Vario EL III spectrometer (Elementar, Germery).

## General Procedure for the One-Pot Reductive Etherification

The reaction mixture of carbonyl compound (2.0 mmol), sodium hydride (2.5 mmol, 0.1 g), and organic halide (2.5 mmol) in 2.5 mL of 1,4-dioxane was stirred under a nitrogen atmosphere at reflux for 6 h. Then the mixture was filter to remove the inorganic salt, and the filtrate was evaporated under reduced pressure to remove the solvent. The residual oil was purified by flash chromatography through a silica-gel columm (ethyl ether/petroleum ether) to afford pure products.

## Data

#### Compound 2f

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.49–2.14 (m, 14H), 3.54 (s, 1H), 4.51 (s, 2H), 7.22–7.36 (m, 5H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OCD<sub>3</sub>) 27.5, 27.5, 31.5, 31.8, 36.3, 37.4, 69.0, 81.0, 126.9, 127.1, 128.1, 139.9. Anal. calcd. for C<sub>17</sub>H<sub>22</sub>O: C, 84.25; H, 9.15. Found: C, 83.85; H, 9.15.

## Compound 2g

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.49–2.12 (m, 14H), 3.53 (s, 1H), 4.50 (s, 2H), 7.21–7.27 (m, 3H), 7.37 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 27.6, 31.8, 31.9, 36.6, 37.7, 68.6, 81.7, 125.4, 127.4, 129.6, 134.3, 141.9. Anal. calcd. for C<sub>17</sub>H<sub>21</sub>OCl: C, 73.76; H, 7.65. Found: C, 73.76; H, 7.90.

## Compound 2h

Light yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.25–2.14 (m, 14H), 3.53 (s, 1H), 3.79 (s, 6H), 4.49 (s, 2H), 6.36 (t, J=2.4 Hz, 1H), 6.54 (s, 1H), 6.55 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 27.5, 31.7, 31.8, 36.6, 37.6, 59.3, 69.2, 81.2, 99.2, 105.1, 142.1, 160.8. Anal. calcd. for C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>: C, 75.46; H, 8.67. Found: C, 75.43; H, 8.62.

## Compound 2i

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.48–2.09 (m, 14H), 3.98 (s, 1H), 4.64 (s, 2H), 7.26–7.63 (m, 3H), 8.54 (d, J = 4.4 Hz, 1H). Anal. calcd.

#### Compound 2j

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.42–2.04 (m, 14H), 3.43 (s, 1H), 3.95 (d, 2H), 5.19 (dd, J=1.6, 8.8 Hz, 1H), 5.27 (dd, J=1.6, 12.0 Hz, 1H), 5.86–5.96 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 27.6, 31.7, 31.9, 36.7, 37.7, 68.5, 81.2, 116.0, 136.0. HRMS (EI) calcd. for C<sub>13</sub>H<sub>20</sub>O M<sup>+</sup>: 192.1514. Found: 192.1515.

#### Compound 2k

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.38–1.96 (m, 14H), 3.26 (s, 1H), 3.27 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 27.4, 27.4, 31.3, 31.4, 36.4, 37.6, 55.2, 83.2. HRMS (EI) calcd. for C<sub>11</sub>H<sub>18</sub>O M<sup>+</sup>: 166.1358. Found: 166.1357.

## Compound 21

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.21 (t, J = 7.2 Hz, 3H), 1.48–2.03 (m, 14H), 3.43 (s, 1H), 3.49 (q, J = 7.2 Hz, 2H);<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 15.6, 27.5, 27.6, 31.3, 31.4, 36.5, 37.6, 64.2, 81.4. HRMS (EI) calcd. for C<sub>12</sub>H<sub>20</sub>O: 180.1514. Found: 180.1523.

## Compound 2m

Light yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.85 (t, J = 7.2 Hz, 3H),  $\delta$  1.29–1.98 (m, 18H), 3.32–3.35 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 13.9, 19.6, 27.5, 31.6, 31.8, 32.4, 36.6, 37.6, 67.0, 81.4. HRMS (EI) calcd. for C<sub>14</sub>H<sub>24</sub>O M<sup>+</sup>: 208.1827. Found: 208.1826.

## Compound 4e

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.66 (s, 3H), 0.81 (s, 3H), 1.60–0.87 (m, 6H), 1.75 (m, 1H), 1.98 (d, J = 3.2 Hz, 1H), 3.25 (d, J = 14.8 Hz, 1H), 3.61 (d, J = 14.8 Hz, 1H), 4.89 (d, J = 11.6 Hz, 1H) 4.97 (d, J = 11.6 Hz, 1H), 7.38–7.12 (m, 10H); MS (API-ES Positive), m/z (M<sup>+</sup>): 332.3. Anal. calcd. for C<sub>24</sub>H<sub>28</sub>O: C, 86.70; H, 8.49. Found: C, 86.67; H, 8.46.

#### Compound **2r**

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.70 (s, 6H), 4.51 (s, 2H), 4.53 (s, 2H), 6.72 (s, 2H), 6.97 (s, 1H), 7.28–7.31 (m, 5H). HRMS (EI) calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>3</sub>: 258.1256. Found: 258.1252.

#### Compound 2s

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.81 (s, 3H), 3.82 (s, 3H), 4.52 (s, 2H), 4.54 (s, 2H), 6.47 (m, 2H), 7.25–7.26 (m, 4H), 7.34 (s, 1H). HRMS (EI) calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>3</sub>Cl: 292.0866. Found: 292.0867.

#### Compound 2t

Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  4.05 (d, J = 1.6 Hz, 2H), 4.17 (d, J = 4.4 Hz, 2H), 5.22 (dd, J = 1.6, 8.8 Hz, 1H), 5.32 (dd, J = 1.6, 15.6 Hz, 1H), 5.91–5.97 (m, 1H), 6.27–6.34 (m, 1H), 6.64 (d, J = 16 Hz, 1H), 7.24–7.40 (m, 5H); HRMS (EI) calcd. for C<sub>12</sub>H<sub>14</sub>O: 174.1055. Found: 174.1052.

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