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# A Facile Synthesis of Aldehyde and Ketone via Sonochemical Barbier Reaction and Oxidation

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Methyl ketone is prepared by a sonochemical Barbier reaction of methyl iodide, magnesium powder and aldehyde in Benzene/THF (9/1) solvent in a commercial ultrasonic cleaning bath (39 kHz), followed by the addition of N-chlorosuccinimide (NCS) as an oxidizing agent.

## INTRODUCTION

The synthesis of unsymmetric ketones, especially methyl ketones, is of importance in organic synthesis.[1-3] Typically, carbonyl compounds are obtained by oxidation of alcohols with chromium or manganese reagents.[4] An alternative method to producing carbonyl moiety is through the cleavage of a metal-oxygen bond by a hydride transfer process.[5-8] In the latter process, the creation of the metal-oxygen bond from simple alcohol is a prerequisite. Based on the studies in our laboratory, we expect that the formation of alkylmagnesium oxide compound ($RCH_2$-OMgBr) can be generated *in situ* from a combination of alcohol ($RCH_2$-OH), magnesium and *n*-butyl bromide under ultrasonic conditions (Scheme I). When a solution of 1-decanol (1 mmol), magnesium powder (1.2 mmol), *n*-butyl bromide (1.2 mmol) in anhydrous THF (4 mL) was sonicated, the magnesium powder disappeared after 5-10 minutes. It showed that Grignard reagent can be generated in the presence of alcohol under ultrasound.[9] It should be noted that alkylmagnesium oxide cannot be generated in the presence of alcohol under reflux.[10] The cleavage of the magnesium-oxygen bond of $RCH_2$-OMgBr was then performed by the addition of N-chlorosuccinimide (NCS) as an oxidizing agent.[6-8]

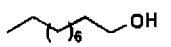
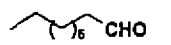
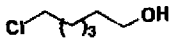
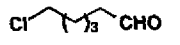
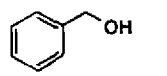
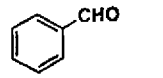
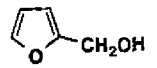
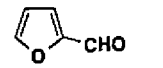
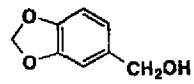
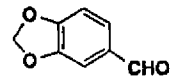
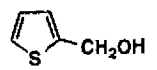
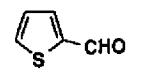
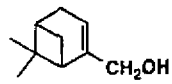
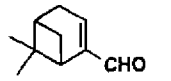
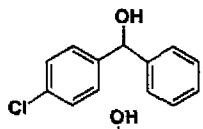
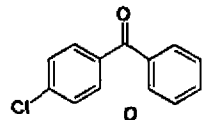
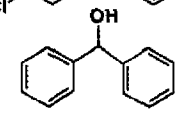
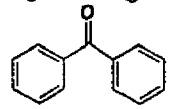
**Scheme I**

$$RCH_2\text{-}OH + Mg + n\text{BuBr} \xrightarrow{))} RCH_2\text{-}OMgBr \xrightarrow{NCS} RCHO$$

## RESULTS AND DISCUSSIONS

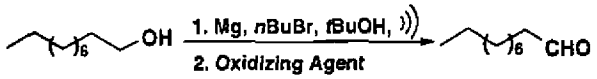
This sonochemical method was applied to the preparations of aldehydes and ketones and the results are shown in Table 1. Several alkyl bromides (*iso*-propyl and *tert*-butyl bromides) were investigated for this Barbier-type deprotonation process and the best results were achieved hy using *n*-butyl bromide. When *tert*-butyl bromide was introduced under this reaction condition, the yield of aldehyde was very low (< 20%).

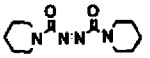
Table 1. Synthesis of Carbonyl via Barbier Deprotonation-Oxidation

| Entry | Substrate | Product | Yield |
|---|---|---|---|
| 1 |  |  | 89% |
| 2 |  |  | 75% |
| 3 |  |  | 79% |
| 4 |  |  | 75% |
| 5 |  |  | 71% |
| 6 |  |  | 64% |
| 7 |  |  | 71% |
| 8 |  |  | 74% |
| 9 |  |  | 82% |

The cleavage of magnesium-oxygen bond by different oxidizing agents was also investigated (Scheme II). The highest yield was achieved when NCS was used as an oxidizing agent. Interestingly, when $PhI(OAc)_2$ and DPAD (1,1′-Azodicarbonyl piperidine) were used for this oxidation step, it must be dissolved in THF beforehand, otherwise the oxidation would not proceed. This Barbier deprotonation-oxidation procedure provides an alternative method for preparation of aldehyde, especially for long chain fatty aldehydes (Table 1, Entry 1) which are difficult to achieve by

**Scheme II**



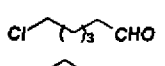
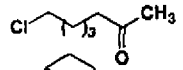
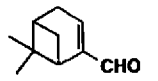
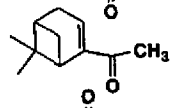
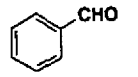
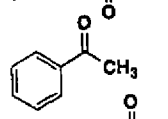
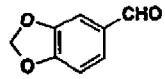
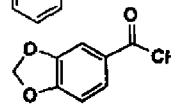
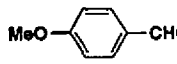
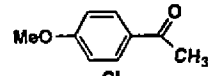
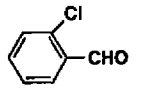
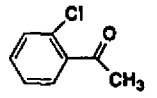
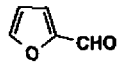
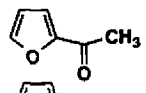
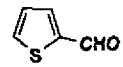
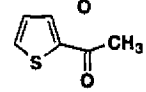
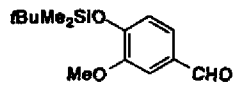
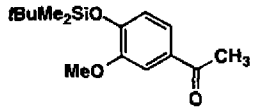

| Oxidizing Agent | Yield |
|---|---|
| NCS | 89% |
| NBS (N-Bromosuccinimide) | 74% |
| $Pb(OAc)_4$ | 72% |
| $PhI(OAc)_2$ | 76% |
| DPAD  | 85% |
| DEAD (Diethyl azodicarboxylate) | mess |
| PDC | 45% |

some typical oxidizing agents.[4,11]

The Barbier reaction has been extensively used to produce alcohol with the addition of alkyl halide to carbonyl compound.[12,13] Thus, we feel that our method can be further applied to synthesizing unsymmetric ketones. Methyl carbonyl moiety has been widely used in natural product synthesis.[14-16] Interestingly, methyl alcohol can not be readily synthesized from the addition of Grignard[17-21] ($CH_3MgI$) or organolithium[22-25] ($CH_3Li$) reagents to aldehyde due to low yields and side reactions. If a solution of benzaldehyde, Mg and methyl iodide in anhydrous THF was sonicated for 10 minutes and then NCS was added for the oxidation process, the expected product methyl ketone was obtained in a very low yield (< 15%) due to the reaction solution became slurry. Fortunately, this problem can be overcome by using mixed solvents. A solution of benzaldehyde, Mg and methyl iodide in benzene/THF (v/v = 9/1)[26] was sonicated for 10 minutes and followed by the treatment of NCS. This one-pot method indeed produced the expected methyl phenyl ketone with a 75% yield (Table 2, Entry 3). In our studies, a series of methyl ketones were synthesized and the results are shown in Table 2.

This one-pot sonochemical reaction provides a convenient procedure for the synthesis of methyl ketones. Other applications in the synthesis of unsymmetrical ketones are underway.

Table 2. *Synthesis of Methyl Ketone*

| Entry | Substrate | Product | Yield |
|---|---|---|---|
| 1 |  |  | 58% |
| 2 |  |  | 64% |
| 3 |  |  | 75% |
| 4 |  |  | 77% |
| 5 |  |  | 70% |
| 6 |  |  | 48% |
| 7 |  |  | 74% |
| 8 |  |  | 68% |
| 9 |  |  | 64% |

## EXPERIMENTAL SECTION

### General

The $^1$H-NMR (proton nuclear magnetic resonance) spectra were recorded at 300 MHz (Bruker-AC300P) with deuteriochloroform ($CDCl_3$, Aldrich 99.8 atom% D) as solvent and internal standard. The $^{13}$C-NMR (carbon nuclear magnetic resonance) spectra were recorded at 75.5 MHz (Bruker-AC300P) with $CDCl_3$ as the solvent and the internal standard. Infrared spectra (IR) were recorded on a BIO-RAD FTS-40 infrared spectrophotometer as a liquid film (neat) or a Nujol mull. Polystyrene was used as a standard, and the spectra are reported in reciprocal centimeters ($cm^{-1}$). Ultraviolet spectra (UV) were reported on a Shimadzu 3101PC spectrophotometer in the indicated solvent, and are reported in nanometers (nm). Mass spectra (MS) were recorded on a JEOL SX-102A and VG 70-250S spectrophotometers and are reported in *m/e* units for the most abundant peaks. All experiments were carried out under a nitrogen atmosphere which was dried primarily by passing through a column of potassium hydroxide (KOH) layered with calcium sulfate ($CaSO_4$). The ultrasonic cleaning bath was filled with water containing 3-5% detergent. In our laboratory, we use Decon 90 which permits much more even cavitation in the bath water. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in a recirculating still prior to use. Hexane and ethyl acetate were distilled from calcium hydride, and benzene was distilled from so-

dium prior to use. Thin-layer chromatography (TLC) analysis were performed on a plastic plate (or aluminum sheet) precoated with silica gel (Merck, 5554 Silica gel $60F_{254}$). Visualization was accomplished by UV light or developed by spraying with a 10% phosphomolybdic acid ethanol solution. Column chromatography was performed using silica gel (Merck 230-400 mesh) and ethyl acetate/hexane mixtures as eluent. Spectral grade purification by high performance liquid chromatography (HPLC) was carried out using a Rheodyne 7000 sample injector, Jasco PU-980 intelligent pumps, Jasco RI-930 Refractive Index Detector and Phenomenex column (Spherex 10 Silica).

**The typical procedure for the oxidation of alkylmagnesium oxide (Scheme II)**

A solution of 1-decanol (1.0 mmol), magnesium powder (2.5 mmol), *n*-butyl bromide (2.4 mmol) and *t*-butyl alcohol[27] (1.0 mmol) in anhydrous THF (5 mL) is sonicated in a commercial ultrasonic cleaning bath (Crest 575-D, 39 kHz). After the reaction is complete (magnesium appears to have dissolved), the oxidizing agent (1.2 mmol) is slowly added at 0 °C. The reaction mixture is warmed to room temperature and stirred for 25 minutes, aqueous 10% $NaHCO_3$ (20 mL) is added and extracted with diethyl ether (3 × 15 mL). The organic layer is then collected, washed with brine (15 mL), dried with $MgSO_4$, filtered, and the organic solvent removed under reduced pressure.

**The general procedure for the preparation of methyl ketone**

A solution of aldehyde (1.0 mmol), magnesium powder (1.5 mmol), methyl iodide (1.5 mmol) in benzene/THF (v/v = 9/1, 2.5 mL) is sonicated for 10 minutes in a commercial ultrasonic cleaning bath (Crest 575-D, 39 kHz). A solution of NCS (1.2 mmol) in 4 mL THF is then added dropwise at 0 °C. After stirring at 0 °C for 5 minutes and at room temperature for 25 minutes, saturated $Na_2S_2O_3 \cdot 5H_2O$ (10 mL) and water (15 mL) are added and extracted with ether (3 × 20 mL). The organic layer is collected, washed with brine (15 mL), dried with $MgSO_4$, filtered, and the organic solvent removed under reduced pressure. Further purification is achieved by silica gel flash chromatography and eluted with ethyl acetate/hexane. The spectral characterization was obtained by HPLC.

**Spectral Data**

All alcohols shown in Table 1 were purchased from Aldrich and Merck and all were used directly without further purification. All aldehydes in Table 2 (except Entries 1 and 9) were commercial products and were used directly without further purification.

**Decyl aldehyde (Table 1, Entry 1)**

A mixture of 1-decanol (1.0 mmol), *t*-BuOH (1.0 mmol), Mg powder (2.5 mmol), *n*-BuBr (2.4 mmol) in anhydrous THF (4 mL) is sonicated for 10 minutes. At the disappearance of the magnesium, a solution of NCS (1.2 mmol) in 4 mL THF is slowly added at 0 °C. The reaction mixture is warmed to room temperature and stirred for 25 minutes, aqueous 10% $NaHCO_3$ (20 mL) is added and extracted with diethyl ether (3 × 15 mL). The organic layer is then collected, washed with brine (15 mL), dried with $MgSO_4$, filtered, and the organic solvent removed under reduced pressure. Purification is achieved by silica gel flash chromatography eluted with ethyl acetate/hexane. The spectral properties are in good agreement with those reported in the literature.[11] $^1$H-NMR: δ 0.88 (3H, t, $J$ = 6.8), 1.16-1.42 (12H, m), 1.59-1.74 (2H, m), 2.41 (2H, dt, $J$ = 9.2, 2.0 Hz), 9.76 (1H, t, $J$ = 2.0 Hz).

**6-Chloro-1-hexanal (Table 1, Entry 2)**

$^1$H-NMR: δ 1.40-1.57 (2H, m), 1.58-1.75 (2H, m), 1.76-1.89 (2H, m), 2.46 (2H, t, $J$ = 7.8 Hz), 3.54 (2H, t, $J$ = 6.9 Hz), 9.77 (1H, s). $^{13}$C-NMR: δ 21.3, 26.4, 32.3, 43.7, 44.7, 202.2. IR (neat): 2941 (s), 2864 (m), 2726 (w), 1722 (s), 1467 (w), 1393 (w), 725 (m), 656 (m) cm$^{-1}$. MS: *m/z* 137 (15, M+2), 135 (77, M), 133 (base), 117 (19), 115 (16), 99 (15), 97 (22), 83 (5), 73 (6), 69 (24), 68 (5), 60 (5), 58 (4), 56 (13).

**7-Chloro-heptan-2-one (Table 2, Entry 1)**

$^1$H-NMR: δ 1.35-1.50 (2H, m), 1.51-1.70 (2H, m), 1.71-1.88 (2H, m), 2.12 (3H, s), 2.44 (2H, t, $J$ = 7.3 Hz), 3.52 (2H, t, $J$ = 6.7 Hz). $^{13}$C-NMR: δ 22.9, 26.3, 29.9, 32.3, 43.6, 44.7, 208.6. IR (neat): 2950 (s), 2863 (w), 1714 (s), 1462 (w), 1373 (m), 1170 (m), 746 (m), 652 (m) cm$^{-1}$. MS: *m/z* 151 (3, M+2), 149 (7, M), 129 (7), 113 (12), 112 (10), 83 (21), 69 (22), 55 (57), 43 (base), 41 (73), 27 (23).

**(1R)-(-)-6,6-Dimethyl-2-formylbicyclo[3.1.1]hept-2-ene (Table 2, Entry 2)**

$^1$H-NMR: δ 0.73 (3H, s), 1.01 (1H, d, $J$ = 9.1 Hz), 1.31 (3H, s), 2.06-2.19 (1H, m), 2.28 (3H, s), 2.36-2.53 (3H, m), 2.95 (1H, t, $J$ = 5.7 Hz), 6.74 (1H, m). $^{13}$C-NMR: δ 20.8, 24.9, 25.8, 31.1, 32.5, 37.3, 39.4, 40.2, 137.4, 149.7, 196.9. IR (neat): 2950 (s), 2927 (s), 1663 (s), 1626 (m), 1415 (w), 1379 (m), 1261 (s), 1052 (w), 813 (w) cm$^{-1}$. UV: ($CH_3CN$) $\lambda_{max}$ = 269 nm (ε 10,380). MS: *m/z* 165 (base, M), 164 (14), 149 (8), 147 (3), 122 (8), 121 (22), 109 (4), 107 (9), 105 (27), 93 (4), 91 (7), 79 (2), 77 (2).

**3',4'-(Methylenedioxy)acetophenone (Table 2, Entry 4)**

$^1$H-NMR: δ 2.44 (3H, s), 5.94 (2H, s), 6.74 (1H, d, $J$ = 8.2 Hz), 7.32 (1H, d, $J$ = 1.7 Hz), 7.45 (1H, dd, $J$ = 8.2, 1.7 Hz). $^{13}$C-NMR: δ 26.1, 101.6, 107.5, 107.6, 124.5, 131.8, 147.9, 151.5, 196.0.

**4'-Methoxyacetophenone (Table 2, Entry 5)**

$^1$H-NMR: δ 2.54 (3H, s), 3.86 (3H, s), 6.92 (2H, d, $J$ = 8.7 Hz), 7.93 (2H, d, $J$ = 8.7 Hz). $^{13}$C-NMR: δ 26.3, 55.4, 113.6, 130.3, 130.5, 163.5, 196.7.

The spectral properties are in good agreement with those reported in the literature.[23]

**2'-Chloroacetophenone (Table 2, Entry 6)**

$^1$H-NMR: δ 2.65 (3H, s), 7.28-7.47 (3H, m), 7.51-7.58 (1H, dd, $J$ = 7.3, 1.7 Hz). $^{13}$C-NMR: δ 30.7, 126.9, 129.4, 130.5, 130.6, 132.0, 139.1, 200.4.

The spectral properties are in good agreement with those reported in the literature.[24]

**2-Acetylfuran (Table 2, Entry 7)**

$^1$H-NMR: δ 2.46 (3H, s), 7.05-7.14 (1H, m), 7.52-7.62 (1H, m), 7.63-7.72 (1H, m). $^{13}$C-NMR: δ 26.8, 128.0, 132.4, 133.6, 144.5, 190.6.

The spectral properties are in good agreement with those reported in the literature.[28]

**2-Acetylthiophene (Table 2, Entry 8)**

$^1$H-NMR: δ 2.54 (3H, s), 7.06-7.15 (1H, m), 7.56-7.64 (1H, m), 7.65-7.70 (1H, m). $^{13}$C-NMR: δ 26.8, 128.0, 132.4, 133.7, 144.5, 190.6.

The spectral properties are in good agreement with those reported in the literature.[29]

**4-*tert*-Butyldimethylsilyloxy-3-methoxybenzaldehyde (Table 2, Entry 9)**

Imidazole (2.6 mmol) and *tert*-butyldimethylsilyl chloride (1.3 mmol) was added to a solution of 4-hydroxy-3-methoxybenzaldehyde (vanillin, Merck, 1.0 mmol) in anhydrous DMF (10 mL) at room temperature under nitrogen atomsphere. The reaction mixture was stirred at room temperature for 12 h and then water (30 mL) was added. The mixture was extracted with diethyl ether (3 × 15 mL) and the organic layer was washed with brine (30 mL), dried ($MgSO_4$), filtered and concentrated. Purification was achieved on a flash chromatograph with silica gel and ethyl acetate/hexane.

$^1$H-NMR: δ 0.19 (6H, s), 1.01 (9H, s), 3.86 (3H, s), 6.96 (1H, d, $J$ = 8.0 Hz), 7.35 (1H, d, $J$ = 9.8 Hz), 7.39 (1H, s), 9.84 (1H, s). $^{13}$C-NMR: δ -4.6, 18.5, 25.6, 55.4, 110.1, 120.7, 126.2, 130.9, 151.3, 151.6, 190.9. IR (neat): 3072 (w), 2935 (s), 2859 (s), 2730 (m), 1700 (s), 1602 (s), 1516 (s), 1468 (s), 1424 (s), 1390 (s), 1292 (s), 1146 (s), 1126 (s), 1038 (s), 904 (s), 845 (m), 789 (s), 726 (s), 663 (m), 598 (m) cm$^{-1}$. UV: ($CH_3CN$) $\lambda_{max}$ = 308 nm (ε 8,790), 272 nm (ε 13,220), 229 nm (ε 17,720), 203 nm (ε 15,190). MS: *m/z* 267 (1, M), 251 (2), 250 (2), 209 (24), 194 (42), 193 (51), 179 (10), 163 (10), 151 (7), 137 (8), 91 (4), 73 (12), 57 (base), 41 (47), 39 (18), 29 (16), 15 (7).

**4'-*tert*-Butyldimethylsilyloxy-3'-methoxyacetophenone (Table 2, Entry 9)**

$^1$H-NMR: δ 0.18 (6H, s), 1.00 (9H, s), 2.55 (3H, s), 3.86 (3H, s), 6.87 (1H, d, $J$ = 8.1 Hz), 7.47 (1H, dd, $J$ = 8.1, 2.0 Hz), 7.51 (1H, d, $J$ = 2.0 Hz). $^{13}$C-NMR: δ -4.6, 18.5, 25.6, 26.2, 55.4, 110.1, 120.2, 123.0, 126.2, 130.9, 151.3, 151.6, 190.9. IR (neat): 2973 (s), 2935 (s), 2882 (s), 1678 (s), 1595 (s), 1526 (s), 1475 (m), 1410 (m), 1370 (m), 1295 (s), 1232 (s), 1254 (m), 960 (s), 830 (s), 820 (s), 640 (m), 620 (m) cm$^{-1}$. UV: ($CH_3CN$) $\lambda_{max}$ = 301 nm (ε 7,870), 268 nm (ε 13,820), 226 nm (ε 20,000), 203 nm (ε 16,710). MS: *m/z* 281 (8, M), 267 (10), 265 (33), 250 (1), 224 (18), 223 (base), 209 (12), 208 (52), 194 (13), 193 (75), 179 (4), 165 (9), 151 (5), 137 (9), 89 (8), 73 (20), 59 (8).

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**Key Words**

Sonochemical; Barbier reaction; Oxidation; Methyl ketone; Ultrasound.

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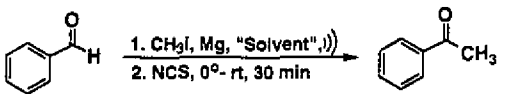


| Solvent (v / v) | Condition | Yield |
|---|---|---|
| THF | Slurry | Low Yield |
| $Et_2O$ | | Low Yield |
| $PhCH_3$ | | N.R. |
| PhH / THF (9 / 1) | | 72% |
| PhH / 2eq. THF | | 70% |
| PhH / THF (8 / 2) | | 70% |
| PhH / THF (7 / 3) | | 64% |
| PhH / THF (5 / 5) | | 62% |

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