Monoanion of the Methyl Ether of 4-Biphenylmethanol (Wittig Rearrangement). The general procedure of Geissman[19] was followed. A dry, 25-mL flask containing 1 g (5 mmol) of ether **16** was capped with a rubber septum and flushed with nitrogen before the addition, via canula, of 10 mL of dry hexane. One equivalent (0.58 g) of TMEDA was then syringed, and the mixture was cooled to -20 °C and then treated with 1 equiv (3.36 mL of a 1.5 M hexane solution) of *n*-butyllithium. The orange-red solution was stirred at room temperature for 6 h and then quenched with 2 N HCl. The aqueous layer was extracted with ether and worked up the usual way. Column chromatography [silica gel, hexane–benzene (50:50) as the eluant] afforded ca. 500 mg of recovered starting material and ca. 400 mg of carbinol **17**: mp 97–98 °C (lit.[20] mp 96.4–97.3 °C); ^{1}H NMR δ 1.50 (d, J = 6, 3, CH_3), 2.10 (s, 1, OH), 4.84 (q, J = 6, 1, CH), 7.2–7.6 (m, 9, aromatic).

4-Biphenylmethanol-α,α-d_2 (14). In a slight modification of the procedure of Brown et al.,[21] 200 mg (ca. 1 mmol) of **6** in 25 mL of dry ethyl ether, at 0 °C, was treated with 76 mg (2 mmol) of lithium aluminum deuteride. The ice–water bath was removed and the reaction mixture heated to reflux for 1 h. Product **14** was then extracted and purified. ^{1}H NMR and MS spectra indicated ca. 100% deuterium present at the benzylic carbon.

1,2-Di-4-biphenyl-1,2-ethanediol (19). 4-Biphenylmethanol (**4**, 278 mg, 1.5 mmol) was dissolved in 25 mL of dry THF and 348 mg (3 mmol) of freshly distilled tetramethylethylenediamine (TMEDA) and treated with 2.2 equiv (2.2 mL of a 1.5 M solution) of *n*-butyllithium. The resulting orange-red solution was heated to reflux for 6 h and then cooled to room temperature (the reaction mixture had turned purple after 4–5 h of reflux). Twenty five milliliters of 1 N HCl was added, and the organic material extracted with ethyl acetate. The usual workup procedure was followed by preparative TLC, with ethyl acetate–chloroform (50:50) as the eluant. Diol **19** (50 mg, 20% yield) was isolated from the lower band, R_f 0.24, and was crystallized from chloroform: mp 217–218 °C; IR (KBr) 3100–3600 (OH) cm^{-1}; ^{1}H NMR δ 3.85 (s, 2, OH), 4.77 (s, 2, CH), 7.2–7.7 (m, 18, aromatic); MS, m/e 348 (M^+ - 18), 184 (M^+ - 182), 183 (M^+ - 183), 181 (M^+ - 185).

Acknowledgment. We are indebted to Professors P. Joseph-Nathan (Instituto Politécnico Nacional), E. L. Eliel (University of North Carolina), and W. F. Bailey (University of Connecticut) for helpful discussions. We are grateful to Professor F. Walls (Instituto de Química, UNAM) for the mass spectra and to Avon Cosmetics for an undergraduate thesis scholarship to A.G.-R.

Registry No. **4**, 3597-91-9; **5**, 5728-52-9; **6**, 92-92-2; **7**, 519-73-3; **8**, 86130-02-1; **14**, 86130-03-2; **16**, 86130-05-4; **17**, 3562-73-0; **19**, 86130-04-3; *n*-butyllithium, 109-72-8; *sec*-butyllithium, 598-30-1; *tert*-butyllithium, 594-19-4; methyllithium, 917-54-4.

(19) Geissman, T. A. *Org. React. (N.Y.)* **1944**, *2*, 94–113.
(20) Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fuji, T.; Yukawa, Y.; Yasubide, Y. *Bull. Soc. Chem. Jpn.* **1975**, *48*, 3337–3346.
(21) Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458–1463.

Oxidation of 2-Methyl-4,5,6,7-tetrahydrobenzofuran with *m*-Chloroperbenzoic Acid

Samuel B. Gingerich and Paul W. Jennings*

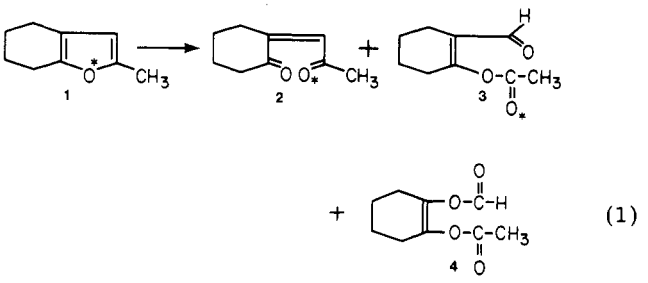
Department of Chemistry, Montana State University, Bozeman, Montana 59717

Received October 26, 1982

The peracid oxidation of 3-methyl-4,5,6,7-tetrahydrobenzofuran and perhydrodibenzofuran has been reported earlier.[1] In these systems, a facile reaction occurred at 0 °C to form an ϵ-lactone in nearly quantitative yield. In this article, we report on the *m*-chloroperbenzoic acid (mCPBA) oxidation of 2-methyl-4,5,6,7-tetrahydrobenzofuran (**1**), which has provided yet another interesting and unique set of products. Further, use of ^{18}O-labeled **1** has provided evidence for its oxidative pathway.

Results and Discussion

Synthesis and Reaction of Compound 1. Compound **1** was readily synthesized in five steps (48% yield) by using standard reactions that were slightly modified as noted in the Experimental Section. It reacted more vigorously than the 3-methyl analogue at 0 °C to form products **2**–**4** as is shown in eq 1. A higher yield of **2** (70%) was obtained



(1)

when 1 equiv of mCPBA was added slowly to a dilute solution of **1** in CH_2Cl_2 at 25 °C. Furthermore, compounds **3** and **4** were also obtained from **1** in higher yields under the proper conditions (see Experimental Section).

Compound **2** was characterized as an enedione by spectral data. Its infrared spectrum indicated carbonyl functionality with a broad absorption at 1690 cm^{-1}, which was further corroborated by ^{13}C NMR spectroscopy with resonances at 204.9 and 200.1 ppm. From the gated decoupled spectra, both of these resonances were shown to be singlets. Specific proton decoupling experiments showed that the ^{13}C resonance at 200.1 ppm was coupled to the methyl hydrogens by 4 Hz and to the olefinic proton by 6 Hz. Another resonance at 150.3 ppm, which was also shown to be a singlet by gated decoupling experiments, was assigned to the olefinic carbon in the six-membered ring. Finally, the resonance at 129.4 ppm, which is a doublet in the gated decoupled spectrum, was assigned to the olefinic carbon bonded to a single hydrogen and the acetyl function. There were five aliphatic carbon resonances at 43.2 (t), 36.3 (t), 29.7 (q), 26.2 (t), and 26.2 (t) ppm, which justifies the methyl group and the four carbons of the cyclohexyl group.

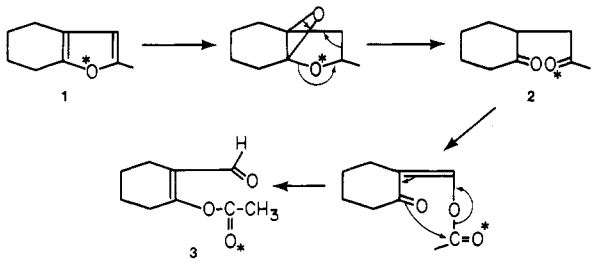
The structure of compound **3** was also justified by spectral data. The aldehydic carbon (1680 cm^{-1}) resonated at 189.1 ppm in the ^{13}C NMR spectrum and was coupled to a single proton by 177 Hz, which is typical. The ester carbonyl carbon and the two olefinic carbons, which were all singlets, had resonances at 168.5, 164.1, and 126.6 ppm, respectively. Further oxidation of compound **3** gave formate **4**, which exhibited ^{13}C NMR shifts of 168.5 (s), 158.5 (d, $^1J_{C-H}$ = 231 Hz), 137.2 (s), and 136.1 (s) ppm. These are consistent with the acetyl ester carbonyl, the formate carbonyl, and the olefinic carbons of **4**. The formation of **4** from compound **3** is extremely facile.

In order to determine the reaction paths for the formation of enedione **2** and ester **3**, we decided to label **1** with ^{18}O. This was readily accomplished by an $H_2{}^{18}O$ exchange reaction with a ketonic intermediate in the synthesis of **1**. The label was located and quantized by NMR and mass spectral methods.[2]

(1) Gingerich, S. B.; Campbell, W. H.; Bricca, C. E.; Jennings, P. W. *J. Org. Chem.* **1981**, *46*, 2589.

0022-3263/83/1948-2606$01.50/0

Scheme I



Oxidation of 1-^{18}O with mCPBA proceeded as described earlier, and the label was determined to be in the cyclohexyl carbonyl oxygen of **2** and in the ester carbonyl oxygen of **3** as shown in eq 1 with an *. Carbon-13 resonances attached to ^{18}O are located approximately 0.05 ppm upfield of the analogous resonance that is bonded to ^{16}O. For compounds **2** and **3**, the chemical shifts for the carbonyl resonances bonded to ^{18}O were 0.05 and 0.04 ppm, respectively. The signal to noise ratio in these NMR spectra was 100:1, which says that we could see any ^{18}O-labeled carbons that were higher than 1%. The amount of label in these compounds was also determined by mass spectroscopy.

Mechanistic Conclusions. Enedione **2** is thought to result from the rearrangement of an intermediate epoxide formed by the reaction of **1** with mCPBA. Since there are two epoxidation sites on furan **1**, we were curious as to which one would be preferentially chosen. The labeling results suggest that the initial epoxidation occurs at the cyclohexyl side of the furan as shown in the first line of Scheme I. This is reasonable on the basis of the concept that epoxidation should occur at the double bond bearing more electron-donating groups.[3]

Ester **3** was assumed to be formed via the well-known Borowitz reaction.[4] In that reaction the enol–ether double bond is cleaved to two carbonyls. However, the ^{18}O labeling results are not consistent with a Borowitz-type reaction since it would have resulted in ^{18}O at the ester oxygen rather than at the ester carbonyl oxygen. Therefore, we proposed that a Baeyer–Villiger oxidation occurs at the methyl ketone with subsequent transfer of the acyl group as shown in the second line of Scheme I.

Precedent for the proposed acyl transfer exists in the work of Lutz[5] and co-workers, who showed that a similar transfer occurred in the oxidation of tetraphenylfuran.

Summary. Through the use of ^{18}O label, the pathway for the mCPBA oxidation of 2-methyl-4,5,6,7-tetrahydrobenzofuran appears to be reasonably well understood. Epoxidation occurs on the more substituted side of the furan system, as expected, and rearranges to form a trialkylated enedione. This intermediate appears then to react in a Baeyer–Villiger oxidation step to form the acetate, which subsequently transfers the acyl group to form compound **3**. A second and facile Baeyer–Villiger oxidation occurs with this aldehyde to yield formate **4**.

Experimental Section

NMR spectra were determined on a Bruker WM 250-MHz spectrometer using tetramethylsilane as an internal standard. In the determination of ^{18}O incorporation by ^{13}C NMR spectroscopy, sweep widths of 500 Hz were typically used. Data was acquired as a 4K block and transformed as an 8K block following a 0.3-Hz exponential multiplication. Mass spectra were obtained from a Varian Mat CH5 spectrometer. IR spectra were recorded on a Beckman IR5A spectrometer. Elemental analyses were performed by Galbraith Labs.

Preparation of 2-Methyl-4,5,6,7-tetrahydrobenzofuran (1). A solution of cyclohexanone (20 g, 204 mmol, Baker) and cyclohexylamine (20 g, 204 mmol, Aldrich) in 150 mL of ether was allowed to stand over 4-Å molecular sieves for 12 h. Filtration and removal of solvent followed by distillation afforded 35.4 g (97%) of the Schiff base **1a** as a white solid: bp 113–115 °C (8 mm) [lit.[6] bp 121–123.4 °C (10 mm)], mp 23–24 °C; ^1H NMR, IR, and mass spectra were identical with those reported;[6] ^{13}C NMR ($CDCl_3$) 170.7 (s), 58.0 (d), 40.4 (t), 34.3 (t), 34.3 (t), 29.1 (t), 28.1 (t), 27.8 (t), 26.4 (t), 26.0 (t), 25.2 (t), 25.2 ppm (t). The magnesium salt of base **1a** (161 mmol) in THF (prepared following literature[7] procedure) was alkylated with 2,3-dichloropropene (17.9 g, 161 mmol, Aldrich). Following acid hydrolysis and extraction with ether, the reaction mixture was distilled to yield 15.8 g (57%) of 2-(2-chloroprop-2-enyl)cyclohexanone (**1b**) as a clear liquid: bp 104–106 °C (10 mm) [lit.[8] bp 86 °C (4 mm)]; ^1H NMR ($CDCl_3$) 5.18 (2 H, d), 2.91 (1 H, dd), 2.7 (1 H, m), 2.5–2.3 (2 H, m), 2.3–2.05 (3 H, m), 1.95–1.8 ppm (1 H, m); IR 1715, 1640, 890 cm^{-1}; mass spectrum, *m/e* 137, M – Cl^+ (100), 93, 67, 55, 41, 39. **1b** (6.6 g, 38.2 mmol) was cyclized to **1** in 15 mL of 90% H_2SO_4 following a literature procedure.[8] Workup followed by chromatography on silica gel (pentane) afforded 4.5 g (87%) of 2-methyl-4,5,6,7-tetrahydrobenzofuran (**1**) as a clear oil: bp 67–69 °C (10 mm) [lit.[9] bp 77–79 °C (17 mm); ^1H NMR[8] ($CDCl_3$) 4.78 (1 H, br s), 2.6–2.5 (2 H, m), 2.45–2.3 (2 H, m), 2.27 (3 H, s), 1.90–1.65 ppm (4 H, m); ^{13}C NMR 149.8 (s), 149.0 (s), 117.6 (s), 106.5 (d), 23.4 (t), 23.4 (t), 23.2 (t), 22.3 (t), 13.5 ppm (q) [In a ^1H-coupled ^{13}C-NMR spectrum the resonances at 149.8 and 149.0 ppm both appeared as multiplets. Specific proton decoupling of the resonance at 5.78 ppm collapsed the peaks at 149.8 ppm to a quartet ($^2J_{C-H}$ = 10 Hz). Similarly, irradiation of the methyl peak at 2.27 ppm collapsed the resonances at 149.8 ppm to a doublet ($^2J_{C-H}$ = 7 Hz)]; IR[8] 1580, 1450, 1260, 1225, 1130, 960, 915, 790 cm^{-1}; mass spectrum, *m/e* M^+ 136, 108 (100).

Oxidation of 1. To a solution of *m*-chloroperbenzoic acid (3.7 g, 21.4 mmol) in 50 mL of CH_2Cl_2, was added 0.5 g of $NaHCO_3$, and the mixture was cooled to 0 °C. A solution of **1** (1.5 g, 10.7 mmol) in 10 mL of CH_2Cl_2 was added over a period of 1 min with stirring. A flocculent precipitate of *m*-chlorobenzoic acid formed within 1 min. Stirring was continued for 10 min at 0 °C. The reaction mixture was then washed with 10% $Na_2S_2O_3$, 5% NaOH, and brine, and dried over $MgSO_4$. Removal of solvent afforded 1.7 g of a yellow oil, which was found to be a mixture of **2** (20%), **3** (45%), and **4** (20%) by ^1H and ^{13}C NMR.

Oxidation of 1 To Yield 2. To a solution of **1** (1.0 g, 7.6 mmol) in 100 mL of CH_2Cl_2 at room temperature was added a solution of *m*-chloroperbenzoic acid (1.3 g, 7.6 mmol, Aldrich, 80–85%) in 40 mL of CH_2Cl_2 over a period of 3 h with stirring. The reaction mixture was washed twice with 5% NaOH and brine and dried over K_2CO_3. Removal of solvent afforded 1.1 g of a yellow oil, which was chromatographed on silica gel. Elution with 1% ethyl acetate in hexane gave material shown to be a mixture of **1** and **3**. Elution with ethyl acetate afforded 0.89 g (77%) of **2** as a yellow oil: ^1H NMR ($CDCl_3$) 5.97 (1 H, br s), 2.85–2.50 (4 H, m), 2.22 (3 H, s), 2.00–1.80 ppm (4 H, m); ^{13}C NMR ($CDCl_3$) 204.6 (s), 200.1 (s), 150.1 (s), 129.6 (d), 43.2 (t), 36.3 (t), 29.7 (q), 26.2 (t), 26.2 ppm (t); IR 1690 (br), 1630 cm^{-1}; mass spectrum, *m/e* M^+ 152, 109 (100). A sample for analysis was purified by bulb-to-bulb distillation; bp 93–99 °C (0.75 mm). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.89; H, 7.88.

Oxidation of 2 to 3. A solution of **2** (0.45 g, 3.31 mmol) in 5 mL of CH_2Cl_2 was added dropwise with stirring to a solution of *m*-chloroperbenzoic acid (0.6 g, 3.6 mmol) in 10 mL of CH_2Cl_2

(2) Vederas, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 374.
(3) House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: New York, 1972; Chapter 6.
(4) (a) Borowitz, I. J.; Williams, G. J.; Gross, L.; Rapp, R. *J. Org. Chem.* **1968**, *33*, 2013. (b) Borowitz, I. J.; Gonis, G.; Kelsey, R.; Rapp, R.; Williams, G. J. *Ibid.* **1966**, *31*, 3032.
(5) Lutz, R. E.; Welstead, W. J., Jr.; Bass, R. G.; Dale, J. I. *J. Org. Chem.* **1962**, *27*, 1111.
(6) Jacobson, R. M.; Raths, R. A.; McDonald, J. H., III. *J. Org. Chem.* **1977**, *42*, 2545.
(7) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178.
(8) Nienhouse, E. J.; Irwin, R. M.; Finni, G. R. *J. Am. Chem. Soc.* **1967**, *89*, 4557.
(9) Morel, T.; Verkade, P. E. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 35.

at 0 °C over a period of 5 min. The reaction was stirred for 15 min and then washed twice with 5% NaOH and brine and dried over $MgSO_4$. Removal of solvent and chromatgraphy on silica gel (ethyl acetate/hexane, 1:99) afforded 0.41 g (93%) of a clear liquid: bp 100–107 °C (0.8 mm); ^1H NMR ($CDCl_3$) 9.93 (1 H, s), 2.50–2.35 (2 H, m), 2.35–2.15 (2 H, m), 2.24 (3 H, s), 1.85–1.60 ppm (4 H, m); ^{13}C NMR ($CDCl_3$) 189.2 (d, J_{C-H} = 178 Hz), 168.6 (s), 164.2 (s), 126.7 (s), 28.8 (t), 22.1 (t), 21.2 (t), 21.1 (t), 20.7 ppm (q); IR 2750, 1760, 1675, 1650, 1365, 1205, 1125 cm^{-1}; mass spectrum, m/e M^+ 168, 126 (100).

Oxidation of 3 to 4. To a solution of **3** (285 mg, 1.70 mmol) in 10 mL of CH_2Cl_2 was added *m*-chloroperbenzoic acid (300 mg, ~1.8 mmol) in one portion. The flask was swirled and allowed to stand at room temperature for 2 h. The reaction mixture was washed twice with 5% NaOH and brine and dried over K_2CO_3. Removal of solvent afforded 0.28 g (91%) of a clear oil: ^1H NMR ($CDCl_3$) 8.01 (1 H, s), 2.35–2.25 (4 H, m), 2.13 (3 H, s), 1.85–1.70 ppm (4 H, m); ^{13}C NMR ($CDCl_3$) 168.3 (s), 158.6 (d, J_{C-H} = 229 Hz), 137.2 (s), 136.1 (s), 26.8 (t), 26.6 (t), 22.3 (t), 22.3 (t), 20.7 ppm (q); IR 1760 (br), 1370, 1220, 1120 cm^{-1}; mass spectrum, m/e M^+ 184, 43 (100). A sample for analysis was prepared by GLC (200 °C 10 ft × 0.25 in., 15% Carbowax). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.53; H, 6.77.

Oxidation of 1 to 3. To a solution of **1** (0.53 g, 3.87 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added dropwise with stirring a solution of *m*-chloroperbenzoic acid (1.3 g ~7.7 mmol) in 30 mL of CH_2Cl_2 over a period of 1.5 h. The reaction was washed with 5% NaOH (two times) and brine and dried over K_2CO_3. Removal of solvent and chromatography on silica gel (ethyl acetate/hexane, 1:99) afforded 0.521 g (80%) of **3** as a clear oil; spectral properties as above.

Oxidation of 1 to 4. To a solution of **1** (0.3 g, 2.19 mmol) in 20 mL of CH_2Cl_2 was added in small portions with swirling *m*-chloroperbenzoic acid (2.3 g, 7.7 mmol) over a period of 1 h. The flask was stored at 0 °C for 12 h. The reaction mixture was washed twice with 5% NaOH and brine and dried over K_2CO_3. Removal of solvent afforded 0.26 g (64%) of **4** as a clear oil; spectral properties as above.

Preparation of ^{18}O-Labeled 2-Methyl-4,5,6,7-tetrahydrobenzofuran (1-^{18}O). A solution of **1b** (603 mg, 4.0 mmol), 75 μL of H_2O (99% ^{18}O, Stohler Isotope Co.), and 2 μL of concentrated HCl in 3 mL of THF (sufficient to solubilize materials) was allowed to stand at room temperature for 12 h. The reaction mixture was poured into H_2O and extracted several times with hexane. The combined hexane extracts were washed with 5% $NaHCO_3$ and brine and dried over K_2CO_3. Removal of solvent afforded 650 mg (95%) of **1b** as a clear oil: ^1H NMR as above; ^{13}C NMR—the resonance at 210.8 ppm could be resolved into two lines with the upfield resonance ($C^{18}O$) shifted by 0.053 ppm. Comparison of relative intensities of these peaks showed 38% incorporation of ^{18}O. Mass spectral analysis showed 37% ^{18}O. The IR spectrum showed peaks at 1705 ($C^{16}O$) and 1675 ($C^{18}O$) cm^{-1}. **1b** (0.64 g, 3.7 mmol) was cyclized as above by using 1.2 mL of 90% H_2SO_4 (prepared by using 97% $H_2{}^{18}O$, MSD Isotopes). Workup afforded 0.37 g (75%) **1** as a clear oil: ^1H NMR and IR as above; mass spectral analysis showed 14% incorporation of ^{18}O; ^{13}C NMR—the resonance at 149.8 ppm could be resolved into two lines with the upfield line shifted by 0.041 ppm (12% ^{18}O). Similarly, the resonance at 149.0 ppm could be resolved with the upfield resonance shifted 0.039 ppm (12% ^{18}O).

Oxidation of 1-^{18}O to 2-^{18}O. The oxidation was carried out as above with 0.461 g of *m*-chloroperbenzoic acid (~2.7 mmol) in 45 mL of CH_2Cl_2 being added to 0.370 g (2.72 mmol) of 1-^{18}O in 100 mL of CH_2Cl_2. The reaction was worked up to yield 0.37 g of a yellow oil. ^{13}C NMR analysis showed the resonance for carbon 2 (204.6 ppm) to be a single line, while that for carbon 1 (200.1 ppm) could be resolved into two lines with the upfield resonance shifted by 0.050 ppm. Comparison of peak intensities showed 9% retention of ^{18}O. It was assumed the remainder of the ^{18}O was lost by exchange in workup.

Oxidation of 2-^{18}O to 3-^{18}O. To a solution of 2-^{18}O (350 mg, 2.30 mmol) in 20 mL of CH_2Cl_2 was added in one portion *m*-chloroperbenzoic acid (435 mg, 2.6 mmol). The flask was swirled and then allowed to stand for 15 min. Workup afforded 0.369 mg of a yellow oil: ^1H NMR as above; ^{13}C NMR showed that the resonance at 168.6 ppm (carbonyl of ester) could be resolved into two peaks with the upfield peak shifted by 0.037 ppm (9% ^{18}O); mass spectral analysis revealed 10% ^{18}O incorporation.

Acknowledgment. We express our gratitude for financial support of this research by Montana State University and the National Science Foundation Grant CHE 7826160.

Registry No. 1, 17392-08-4; 1-^{18}O, 86014-41-7; **1a**, 10468-40-3; **1a**·Mg, 86014-42-8; **1b**, 17392-07-3; **2**, 86014-43-9; 2-^{18}O, 86014-44-0; **3**, 14713-97-4; 3-^{18}O, 86014-45-1; **4**, 86014-46-2; cyclohexanone, 108-94-1; cyclohexylamine, 108-91-8; 2,3-dichloropropene, 78-88-6.

Convenient Ketone Synthesis by the Reaction of Organocuprate Reagents with 2-Pyridyl Esters

Sunggak Kim* and Jae In Lee

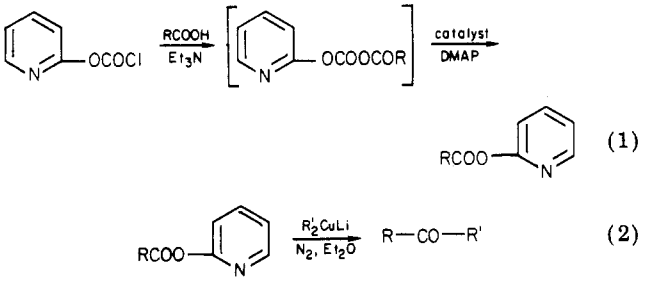
Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea

Received November 9, 1982

Many reports on the synthesis of ketones from organometallic reagents and carboxylic acid derivatives have appeared.[1] Among many available synthetic methods on the synthesis of ketones, reaction of Grignard reagents with acid chlorides[2] or *S*-2-pyridyl thioates[3] and of organocuprate reagents with acid chlorides[4] or thiol esters[5] are the most efficient and the most convenient. However, each method suffers from operational problems and limits with regard to scope.

It has been reported that reaction of Grignard reagents[6] and (π-allyl)nickel halides[7] with 2-pyridyl esters affords ketones and β,γ-unsaturated ketones, respectively. However, reaction of organocuprate reagents with 2-pyridyl esters has not been investigated.[8]

We now report the use of a new reagent, 2-pyridyl chloroformate, for conversion of acids to 2-pyridyl esters (eq 1) and our results for the reaction of lithium dialkylcuprates with 2-pyridyl esters, which gives the corresponding ketones in high yields (eq 2).



2-Pyridyl esters were prepared by a modification of a known method.[9] 2-Pyridyl chloroformate was conven-

(1) (a) Shirley, D. A. *Org. React. (N.Y.)* **1954**, *8*, 28. (b) Jorgensen, M. J. *Ibid.* **1970**, *18*, 1.
(2) Sato, F.; Inoue, M.; Oguro, K.; Sato, M. *Tetrahedron Lett.* **1979**, 4303.
(3) Mukaiyama, T.; Araki, M.; Takei, H. *J. Am. Chem. Soc.* **1973**, *95*, 4763.
(4) (a) Posner, G. H.; Whitten, C. E. *Tetrahedron Lett.* **1970**, 4647. (b) Dubois, J.-E.; Boussu, M.; Lion, C. *Ibid.* **1971**, 829. (c) Posner, G. H.; Whitten, C. E.; McFarland, P. E. *J. Am. Chem. Soc.* **1972**, *94*, 5106.
(5) (a) Anderson, R. J.; Henrick, C. A.; Rosenblum, L. D. *J. Am. Chem. Soc.* **1974**, *96*, 3654. (b) Kim, S.; Lee, J. I.; Chung, B. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 1231.
(6) Araki, M.; Sakata, S.; Takei, H.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1777.
(7) Onaka, M.; Goto, T.; Mukaiyama, T. *Chem. Lett.* **1979**, 1483.
(8) Although conversion of certain esters into ketones by using excess organocuprate reagents has been noted, esters have been known to be generally inert to organocuprate reagents at −78 °C. (a) Humphrey, S. A.; Herrmann, J. L.; Schlessinger, R. H. *J. Chem. Soc. D* **1971**, 1244. (b) Posner, G. H.; Brunell, D. J. *J. Chem. Soc., Chem. Commun.* **1973**, 907.
(9) Corey, E. J.; Clark, D. A. *Tetrahedron Lett.* **1979**, 2875.

0022-3263/83/1948-2608$01.50/0