then (*Z*)-**7b** was distilled (62% from **5b**): bp 146 °C; ^{1}H NMR ($CDCl_3$) δ 0.5–2.5 (11 H, c-C_6H_{11}), 6.13 (ddd, 1 H, $^2J_{HF}$ = 74, $^3J_{HF}$ = 18, $^4J_{HH}$ = 1 Hz, =CHF); ^{19}F NMR ($CDCl_3$) ϕ 138 (m, 1 F, $^3J_{FH}$ = 18, 15, $^3J_{FF}$ = 11 Hz, c-$C_6H_{11}CF$=), 168.3 (ddd, 1 F, $^2J_{FH}$ = 74, $^3J_{FF}$ = 11, $^4J_{FH}$ = 3.8 Hz, =CHF); IR (CCl_4) 1718 cm^{-1}. Anal. Calcd for $C_8H_{12}F_2$: C, 65.73; H, 8.27; F, 25.99. Found: C, 66.06; H, 8.50; F, 26.07.

(*Z*)-3,3-Dimethyl-1,2-difluorobutene (6c). To a solution of 2.5 g (22 mmol) of potassium *tert*-butoxide in 3 mL of dimethyl sulfoxide was added a solution of 1.7 g (12.1 mmol) of **5c** in 1 mL of Me_2SO. The mixture was heated, with stirring, for 48 h at 70 °C. After cooling, the mixture was submitted to a bulb-to-bulb distillation (room temperature, 0.01 mm). The distillate was shaken with excess water in a separatory funnel and the upper layer dried on 4-Å molecular sieves, affording (*Z*)-**6c** (45% from **5c**): bp 81–82 °C (Siwoloboff's method); ^{1}H NMR ($CDCl_3$) δ 1.07 (d, 9 H, $^4J_{HF}$ = 0.5 Hz, CH_3), 6.16 (dd, 1 H, $^2J_{HF}$ = 75, $^3J_{HF}$ = 17.5 Hz, =CHF); ^{19}F NMR ($CDCl_3$) ϕ 140 (ddm, 1 F, $^3J_{FH}$ = 17.5, $^3J_{FF}$ = 10, $^4J_{FH}$ = 0.5 Hz, *t*-BuCF=), 170.2 (dd, 1 F, $^2J_{FH}$ = 75, $^3J_{FF}$ = 10 Hz, =CHF); IR (CCl_4) 1708 cm^{-1}; no analysis; mass spectrum (70 eV), *m/e* 120.

(*Z*)-1-Phenyl-1,2-difluoroethylene (6d) was prepared from **5d** (25 mmol) in a similar manner as was **6a** except that the mixture of **5d** in *t*-BuOH–*t*-BuOK was heated only 3 h at 100 °C. The crude oil was submitted to bulb-to-bulb distillation [60 °C (0.005 mm)]. The most volatile part was distilled in a small Vigreux apparatus to afford 1.15 g (about 30% from **5d**) of (*Z*)-**6d** (contaminated by 9% **5d**): bp 86–87 °C (60 mm) [lit.[7] bp 88–90 °C (60 mm)]; ^{1}H NMR ($CDCl_3$) δ 6.78 (dd, 1 H, $^2J_{HF}$ = 71, $^3J_{HF}$ = 17 Hz, =CHF), 7.18 (s, 5 H, Ph); ^{19}F NMR ($CDCl_3$) ϕ 145.8 (dd, 1 F, $^3J_{FH}$ = 17, $^3J_{FF}$ = 11.5 Hz, PhCF=), 168.8 (dd, 1 F, $^2J_{FH}$ = 71, $^3J_{FF}$ = 11.5 Hz, =CHF); IR (CCl_4) 1693 cm^{-1}; mass spectrum (70 eV), *m/e* 140.

The residue of the bulb-to-bulb distillation was 8: ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9 H, CH_3), 6.28 (d, 1 H, $^3J_{HF}$ = 21 Hz, =CHO-*t*-Bu), 7.12 (5 H, Ph); ^{19}F NMR ($CDCl_3$) ϕ 141.3 (d, $^3J_{FH}$ = 21 Hz, PhCF=); IR (CCl_4) 1678 cm^{-1}.

Epoxidation with *m*-Chloroperoxybenzoic Acid (MCPBA). Typical Procedure. *cis*-1-(1-Adamantyl)-1,2-difluoro-1,2-epoxyethane (9a). To a solution of 2.43 g (14 mmol) of MCPBA in 22 mL of chloroform was added 1.5 g (7.6 mmol) of **6a** in 4 mL of $CHCl_3$. The mixture was stirred overnight at room temperature (although 3 h proved to be sufficient for completion) and then filtered. The solution was washed with 2 mL of 20% sodium bisulfite solution, three 5-mL portions of saturated $NaHCO_3$ solution, and 10 mL of saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. Bulb-to-bulb distillation of the residue (0.005 mm, bath temperature 90 °C) afforded 1.32 g of **9a**: oil (81% from **6a**); ^{1}H NMR ($CDCl_3$) δ 1.52–2.17 (15 H, 1-adamantyl), 5.33 (dd, 1 H, $^2J_{HF}$ = 82.5, $^3J_{HF}$ = 1.8 Hz, >CHF); ^{19}F NMR ($CDCl_3$) ϕ 155.8 (dd, 1 F, $^3J_{FF}$ = 36.7, $^3J_{FH} \simeq$ 1 Hz, AdCF<), 159.6 (dd, 1 F, $^2J_{FH}$ = 82.5, $^3J_{FF}$ = 36.7 Hz, >CHF). Anal. Calcd for $C_{12}H_{16}F_2O$: C, 67.26; H, 7.53; F, 17.73. Found: C, 67.15; H, 7.57; F, 17.51.

***cis*-1-Cyclohexyl-1,2-difluoro-1,2-epoxyethane (9b)** was prepared in a similar manner as was **9a** (72% after bulb-to-bulb distillation), bp 180–182 °C (Siwoloboff's method). ^{1}H and ^{19}F NMR data are in agreement with those previously reported.[1] Anal. Calcd for $C_8H_{12}F_2O$: C, 59.25; H, 7.46. Found: C, 59.46; H, 7.61.

***cis*-3,3-Dimethyl-1,2-difluoro-1,2-epoxybutane (9c)** was prepared in the same way as was **9a** (starting from 0.3 g of **7c**) except that the whole chloroform solution was first submitted to bulb-to-bulb distillation and then the solvent was removed by distillation on a Vigreux column, leaving **9c** (55%): bp 100–101 °C (Siwoloboff's method); no analysis; mass spectrum (70 eV), *m/e* 136. ^{1}H and ^{19}F NMR data are in agreement with those previously reported.[1]

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Registry No. 3a, 5122-82-7; **3b**, 56077-28-2; **3c**, 5469-26-1; **3d**, 70-11-1; **4a**, 75600-43-0; **4b**, 768-04-7; **4c**, 4538-80-1; **4d**, 450-95-3; **5a**, 75600-44-1; **5b**, 75600-45-2; **5c**, 58384-37-5; **5d**, 75600-46-3; **6a**, 75600-47-4; **6b**, 75600-48-5; **6c**, 58384-38-6; **6d**, 15480-90-7; **8**, 75600-49-6; **9a**, 75600-50-9; **9b**, 75600-51-0; **9c**, 75600-52-1.

Remarkable Stereoselectivity in the Reaction of Nucleophilic Reagents with C(7) Carbonyl Derivatives of Functionalized Bicyclo[2.2.1]heptanes

George Majetich, Paul A. Grieco,*[1] and Shannon Bongers

Department of Chemistry, University of Pittsburgh Pittsburgh, Pennsylvania 15260

Mary G. Erman and David A. Langs*

Medical Foundation of Buffalo, Buffalo, New York 14203

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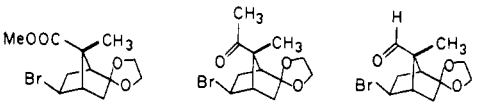
This paper describes a series of noteworthy reactions on the rigid bicyclo[2.2.1]heptane derivatives **1–3**.

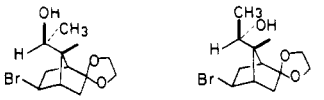


1 **2** **3**

In general, carboxylic esters react rapidly with organometallic reagents (e.g., CH_3Li, CH_3MgI) to form tertiary alcohols in high yield. There are, however, several reports in the literature describing the synthesis of ketones in good yield by the reaction of organolithium reagents with hindered esters.[2] Bulky organolithium reagents are known to react with aromatic esters to produce ketones in good yield.[3] With respect to Grignard reagents, it has been demonstrated that bulky alkylmagnesium halides in hexamethylphosphoramide react with hindered esters to afford, upon workup, modest to good yields of ketones.[4]

We have observed that treatment of bromo ketal ester **1**[5] with excess methyllithium (5.0 equiv) in ether gave rise to methyl ketone **2**: mp 70–71 °C; 94% yield. No tertiary alcohol could be detected. The presence of the bulky exo-oriented bromo substituent and the quaternary nature of the C(7) carbon atom of the bicyclo[2.2.1]heptane system are undoubtedly responsible for the observed result. The inability of sodium borohydride to reduce ketone **2** at room temperature further attests to the severe steric hindrance about the C(7) acetyl unit.

In contrast to the results with sodium borohydride, the more reactive *lithium aluminum hydride smoothly reduced ketone 2 at −20 °C, giving rise to a single crystalline diastereomer* (**4**; mp 127.0–127.5 °C) in 91% yield. NMR analysis ($CDCl_3$) of the product (**4**) revealed a three-proton



4 **5**

doublet centered at δ 1.18 (J = 6 Hz) and a three-proton

(1) Address correspondence to this author at the Department of Chemistry, Indiana University, Bloomington, IN 47405.

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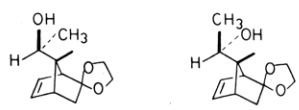
Figure 1. Stereoview of a single molecule of alcohol **4**.

singlet located at δ 1.26. Upon reduction of **2** at room temperature, less than 1% of the isomeric alcohol **5** [NMR ($CDCl_3$) δ 1.20 (s, 3 H), 1.23 (d, 3 H, J = 6 Hz)] could be detected.

Being unable to assign with any degree of certainty a configuration to the newly generated chiral center, we turned to single-crystal X-ray analysis. Alcohol **4** crystallized in space group $R\bar{3}$ with unit cell constants a = 26.639 (1) Å, c = 89776 (5) Å, V = 5517.5 (2) Å^3, and Z = 18. Integrated intensities for 1685 independent reflections with $2\theta \leq 115°$ were measured on a Syntex P3/F diffractometer using Cu Kα radiation. Of these, 1468 were considered observable above background radiation levels ($I \geq 2\sigma I$). The average intensity of five chosen reference standard reflections experienced a linear time-dependent decay approaching 50% during the period of the data collection. The crystal structure was determined by Fourier procedures and refined by full-matrix least-squares methods. Hydrogen atom parameters were included into the structure factor calculations at chemically idealized positions computed from the molecular skeleton. The hydrogen parameters were assigned isotropic thermal parameters and not refined. Anisothermal refinement of the nonhydrogen parameters of the structure converged to a residual of 0.069 for the 1468 observed data. Figure 1 depicts the chirality at the newly created center relative to the handedness of the molecule.

Reaction of bromo alcohol **4** with DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) in refluxing toluene provided the bicyclo[2.2.1]heptene derivative **6**. It is of interest to note



6 **7**

that when ketone **2** was subjected to the reverse sequence of reactions [(1) DBU, xylene, reflux; (2) $LiAlH_4$, THF] there was obtained a 1:1 mixture of alcohols **6** (R_f 0.42; hexanes–ether, 1:2) and **7** (R_f 0.26) which could be readily separated on silica gel chromatography.

During the course of this investigation we examined the reaction of aldehyde **3** with methyllithium. Addition of an ethereal solution of methyllithium to aldehyde **3** (prepared by Collins oxidation of the corresponding alcohol[5]) in ether cooled to –78 °C gave rise to an 83% isolated yield of diastereomer **4** (R_f 0.52; ether–hexane, 1:1) and 10% of the isomeric alcohol **5** (R_f 0.18).

The high stereoselectivity observed in the transformations **1** → **2**, **2** → **4**, and **3** → **4** is indeed remarkable. The formation of diastereomer **4** by either reduction of methyl ketone **2** or addition of methyllithium to aldehyde **3** indicates that there is hindered rotation about the C(7)–C(9) carbon–carbon bond in both **2** and **3**. The above observation further suggests that in the most stable conformation the oxygen atom in substrate **2** resides between the bromine atom and the C(1)–C(7) bond. Since delivery of a hydride can only occur from the top of the molecule, one observes complete specificity. With regard to aldehyde **3**, the preferred orientation of the oxygen atom must be reversed, thus placing the hydrogen atom of the formyl group between the bromine and the C(1)–C(7) bond.

Experimental Section

Melting points were determined on a Fisher-Johns hot stage melting point apparatus. All melting points and boiling points are uncorrected. Infrared (IR) spectra were determined on a Perkin-Elmer 247 grating infrared spectrometer and nuclear magnetic resonance (NMR) spectra were recorded at either 60 MHz (T-60 spectrometer) or at 90 MHz (EM 390) as indicated. Chemical shifts are reported in parts per million (δ) relative to Me_4Si (δ_{Me_4Si} 0.0) as an internal standard. Low-resolution mass spectra were recorded on an LKB-9000 spectrometer. High-resolution spectra were recorded on a Varian MAT CH-5DF instrument. Microanalyses were performed by Galbraith Laboratories, Inc.

Reactions were run under an atmosphere of nitrogen. "Dry" solvents were dried immediately before use. Tetrahydrofuran was distilled from lithium aluminum hydride. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride. Diethyl ether was distilled from sodium. Methylene chloride was passed through a column of alumina prior to use. Silica gel 60 [particle size 0.063–0.200 mm, 70–230 mesh ASTM) was purchased from E. Merck.

7-Acetyl-5-bromo-7-methylspiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane] (2). A solution of bromo ester **1**[5] (10.3 g, 33.7 mmol) in 150 mL of anhydrous ether cooled to 0 °C was treated dropwise with 31.6 mL (50.6 mmol) of a 1.6 M solution of methyllithium in ether. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was quenched with a saturated aqueous solution of ammonium chloride, diluted with ether, washed with brine, and dried over anhydrous magnesium sulfate. The solvent was evaporated in vacuo, and the crude ketone was chromatographed on 350 g of silica gel. Elution with 2:1 hexanes–ether provided 9.07 g (93%) of crystalline ketal ketone **2**: mp 69–70 °C: R_f 0.45 (hexanes–ether, 2:1); IR (CCl_4) 2980, 2890, 1708, 1475, 1455, 1440, 1420, 1388, 1358, 1330, 1314, 1278, 1246, 1220, 1182, 1163, 1105, 1080, 1060, 1040, 1025, 1010, 950, 900 cm^{-1}; NMR (CCl_4) δ 3.5–4.1 (m, 5 H), 2.1–2.8 (m, 5 H), 2.21 (s, 3 H), 1.55 (d, 1 H, J = 14 Hz), 1.36 (s, 3 H); high-resolution mass spectrum calcd for $C_{12}H_{17}BrO_3$ m/e 288.0361, found m/e 288.0367. Recrystallization from ether–hexanes gave analytically pure **2**, mp 70–71 °C. Anal. Calcd for $C_{12}H_{17}BrO_3$: C, 49.84; H, 5.93. Found: C, 50.07; H, 6.02.

Reduction of Bromo Ketone 2 with Lithium Aluminium Hydride. To a suspension of 118 mg (3.11 mmol) of lithium aluminium hydride in 4 mL of anhydrous ether at –20 °C was added dropwise a solution of 600 mg (2.07 mmol) of ketone **2** in 3 mL of anhydrous ether. The reaction mixture was stirred at –20 °C for 3 h. The reaction was quenched with reagent grade ("wet") ether and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure gave crude material which was chromatographed on 30 g of silica gel. Elution with 2:1 hexanes–ether afforded 550 mg (91%) of a single crystalline alcohol (**4**, mp 127.0–127.5 °C) which was homogeneous by TLC analysis: R_f 0.42 (2:1 hexanes–ether, two developments); IR ($CHCl_3$) 3600, 2990, 2880, 1475, 1460, 1440, 1390, 1375, 1340, 1321, 1300, 1270, 1240, 1205, 1145, 1080, 1055, 1040, 1020, 1000, 965, 945, 925, 904, 888, 871, 850 cm^{-1}; NMR (90 MHz) $CDCl_3$ δ 4.80 (br q, 1 H, J = 6 Hz, CHOH), 4.15 (dd, 1 H, J = 5, 9 Hz, CHBr), 3.6–3.9 (m, 4 H, OCH_2CH_2O), 2.61 (dd, 1 H, J = 9, 16 Hz, C(6) endo proton), 2.41 (m, 2 H), 2.17 (dt, 1 H, J = 5, 16 Hz, C(6) exo proton), 1.81 (m, 2 H), 1.53 (d, 1 H, J = 14 Hz, C(3) endo proton), 1.26 (s, 3 H), 1.18 (d, 3 h, J = 6 Hz); high-resolution mass spectrum calcd for $C_{12}H_{19}BrO_3$ m/e 290.0517, found m/e 290.0523. Anal. Calcd for $C_{12}H_{19}BrO_3$: C, 49.50; H, 6.58. Found: C, 49.41; H, 6.53.

α,7-Dimethylspiro[bicyclo[2.2.1]hept-5-en-2,2'-[1,3]dioxolane]-7-methanol (6). A solution of 462 mg (1.59 mmol) of bromo alcohol **4** and 2.42 g (16.0 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene in 20 mL of toluene was refluxed (bath tem-

perature 135 °C) for 23 h. The reaction mixture was cooled to room temperature and chromatographed on silica gel. Elution with 2:1 hexanes–ether afforded 322 mg (97%) of crystalline olefinic alcohol **6**: mp 81.0–82.0 °C; R_f 0.42 (hexanes–ether, 1:2); IR (CCl_4) 3640, 3525, 3070, 2980, 2890, 1632, 1478, 1460, 1442, 1390, 1378, 1350, 1325, 1301, 1263, 1240, 1210, 1160, 1108, 1082, 1050, 1020, 950, 921, 898 cm^{-1}; NMR (CCl_4) δ 6.3–5.8 (m, 2 H, CH=CH), 4.21 (q, 1 H, J = 6 Hz, CHOH), 4.1–3.5 (m, 4 H), 2.66 (br s, 1 H), 2.3–1.9 (m, 2 H), 1.43 (d, 1 H, J = 12 Hz, C(3) endo proton), 1.38 (br s, 1 H, OH), 1.10 (s, 3 H), 1.98 (d, 3 H, J = 6 Hz); high-resolution mass spectrum calcd for $C_{12}H_{18}O_3$ m/e 210.1256, found m/e 210.1260. Recrystallization from hexanes–ether provided analytically pure **6**, mp 82.5–83.5 °C. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.46; H, 8.72.

Preparation and Reduction of 7-Acetyl-7-methylspiro-[bicyclo[2.2.1]hept-5-en-2,2'-[1,3]dioxolane]. A solution of 10 g (34.6 mmol) of keto bromide **2** in 300 mL of xylene containing 52.6 g (0.35 mol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) was refluxed (bath temperature 160 °C). After 17 h, an additional 26.3 g (0.17 mol) of DBU was added, and heating was continued for 4 h. The reaction mixture was cooled to room temperature, diluted with 100 mL of benzene, washed with brine, and condensed under reduced pressure. Chromatography on 1.0 kg of silica gel using 2:1 hexanes–ether gave 6.84 g (95%) of 7-acetyl-7-methylspiro[bicyclo[2.2.1]hept-5-en-2,2'-[1,3]dioxolane]: R_f 0.57 (hexanes–ether, 1:1); IR (CCl_4) 3070, 2970, 2880, 1705, 1630, 1452, 1435, 1420, 1375, 1348, 1320, 1301, 1278, 1260, 1235, 1214, 1208, 1165, 1154, 1105, 1081, 1046, 1010, 973, 945, 915, 890, 870, 855 cm^{-1}; NMR (CCl_4) δ 6.3–5.8 (m, 2H, CH=CH), 4.0–3.6 (m, 4 H, OCH_2CH_2O), 2.82 (br s, 1 H), 2.65 (m, 1 H), 2.02 (dd, 1 H, J = 4, 13 Hz, C(3) exo proton), 1.91 (s, 3 H, CH_3CO), 1.52 (d, 1 H, J = 13 Hz, C(3) endo proton), 1.18 (s, 3 H); high-resolution mass spectrum calcd for $C_{12}H_{16}O_3$ m/e 208.1099, found m/e 208.1103. An analytical sample was prepared by distillation [61–70 °C (bath temperature; 2.5 mmHg)]. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 68.94; H, 7.73.

To a suspension of 1.37 g (36.1 mmol) of lithium aluminium hydride in 75 mL of anhydrous tetrahydrofuran cooled to 0 °C was added a solution of 5.0 g (24.0 mmol) of the above ketone in 25 mL of dry tetrahydrofuran. The reaction mixture was warmed to room temperature after the addition was complete. After 8 h, the reaction mixture was quenched at 0 °C with reagent grade ether and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo left 5.0 g (99%) of a crude mixture (1:1) of alcohols **6** [R_f 0.42 (hexanes–ether, 1:2)] and **7** (R_f 0.26). Chromatography on silica gel using 1:1 hexanes–ether provided in order of elution 2.38 g of crystalline **6** (mp 82.5–83.5 °C), identical in all respects with the sample of **6** prepared above, and 2.35 g of **7**: bp 84–90 °C (bath temperature; 0.45 mmHg); IR (CCl_4) 3640, 3525, 3070, 2980, 2880, 1635, 1475, 1445, 1390, 1376, 1345, 1324, 1301, 1240, 1210, 1151, 1110, 1080, 1048, 1018, 1008, 950, 920, 899 cm^{-1}; NMR (CCl_4) δ 6.1–5.9 (m, 2 H, CH=CH), 4.21 (q, 1 H, J = 6 Hz, CHOH), 4.1–3.5 (m, 4 H), 2.50 (m, 1 H), 2.21 (m, 1 H), 2.05 (dd, 1 H, J = 13, 4 Hz, C(3) exo proton), 1.42 (d, 1 H, J = 13 Hz, C(3) endo proton), 1.13 (s, 3 H), 0.96 (d, 3 H, J = 6 Hz); high-resolution mass spectrum calcd for $C_{12}H_{18}O_3$ m/e 210.1256, found m/e 210.1250. Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.67; H, 8.65.

Preparation of Aldehyde 3. A solution of 0.90 g (3.3 mmol) of 5-bromo-7-methylspiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-7-methanol[5] in 10 mL of dry methylene chloride was added to 3.3 g (33 mmol) of chromium trioxide in 70 mL of dry methylene chloride containing 5.2 g (66 mmol) of pyridine. After 15 min at room temperature the reaction mixture was diluted with reagent grade ether and filtered through anhydrous magnesium sulfate. The filtrate was washed with dilute hydrochloric acid, sodium bicarbonate solution, and saturated sodium chloride solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave crude aldehyde which was chromatographed on 50 g of silica gel. Elution with 4:1 hexanes–ether provided 807 mg (88%) of pure aldehyde: IR ($CHCl_3$) 2955, 2920, 2870, 2800, 2700, 1710, 1445, 1430, 1385, 1370, 1340, 1305, 1280, 1255, 1240, 1220, 1168, 1155, 1141, 1100, 1075, 1050, 1010, 998, 985, 940, 918, 900, 885, 860, 825 cm^{-1}; NMR (CCl_4 90 MHz) δ 9.75 (s, 1 H, CHO), 3.6–4.1 (m, 5 H), 2.0–2.7 (m, 5 H), 1.60 (d, 1 H, J = 14 Hz), 1.22 (s, 3 H).

Reaction of Aldehyde 3 with Methyllithium. A solution of 359 mg (1.30 mmol) of aldehyde **3** in 7.0 mL of anhydrous ether cooled to −78 °C was treated with 2.33 mL (3.25 mmol) of a 1.4 M solution of methyllithium in ether. After 1.5 h at −78 °C, the reaction was quenched by the addition of an aqueous saturated solution of ammonium chloride and diluted with ether. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. Purification of the crude product on silica gel with 5:1 hexane–ether gave in order of elution 314 mg (83%) of pure alcohol **4** (mp 127–129 °C), identical in all respects (NMR, IR, melting point, mixture melting point, TLC) with a sample of **4** prepared above, and 37 mg (10%) of alcohol **5**: IR ($CHCl_3$) 3620, 3400, 2970, 2880, 1480, 1460, 1440, 1380, 1325, 1200, 1140, 1075, 1055, 1015, 1005, 970, 950, 930, 908, 885 cm^{-1}; NMR ($CDCl_3$) 4.80 (q, 1 H, J = 6 Hz), 3.7–4.2 (m, 5 H), 2.2–2.6 (m, 3 H), 2.0–2.2 (m, 2 H), 1.50 (d, 1 H, J = 14 Hz), 1.23 (d, 3 H, J = 6 Hz), 1.20 (s, 3 H).

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Registry No. 1, 75521-01-6; 2, 75521-02-7; 3, 75476-75-4; 4, 75476-76-5; 5, 75521-03-8; 6, 75521-04-9; 7, 75521-05-0; 7-acetyl-7-methylspiro[bicyclo[2.2.1]hept-5-en-2,2'-[1,3]dioxolane], 75476-77-6; 5-bromo-7-methylspiro[bicyclo[2.2.1]heptane-2,2'-[1,3]dioxolane]-7-methanol, 75521-06-1.

A New Synthesis of α-Keto Esters and Acids

Jonathan S. Nimitz and Harry S. Mosher*

Department of Chemistry, Stanford University, Stanford, California 94305

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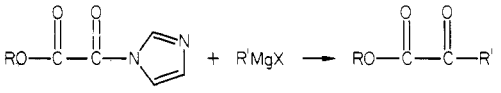
α-Keto acids have been studied extensively because of their widespread distribution in living organisms. However, general methods for synthesis of α-keto acids and α-keto esters are few,[1] and these often involve several nonconvergent steps. We wished to develop a reagent for direct, one-step formation of α-keto esters with a variety of substituents. Futhermore, we wanted to obtain the *tert*-butyl esters so that acid-catalyzed cleavage could readily give the keto acids.[2] The imidazolides **1** and **2**



1, R = Et
2, R = *t*-Bu

appeared promising for this purpose because of the high reactivity of acylimidazolides[3] toward Grignard reagents to yield ketones without significant further reaction to give tertiary alcohols.

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