Table II. Reaction of $C_6H_5O(CH_2)_nBr$ with Mg*

	reagent	temp, °C	time	substrate	product	yield, %
I	$C_6H_5O(CH_2)_3Br$	20	5 min	CO_2	C_6H_5OH	100[a] 71[b]
I		−78	1 h	CO_2	$C_6H_5O(CH_2)_3CO_2H$	71[b]
III	$C_6H_5O(CH_2)_4Br$	20	15 min	CO_2	$C_6H_5O(CH_2)_4CO_2H$	89[b]
IV	$C_6H_5O(CH_2)_5Br$	20	15 min	CO_2	$C_6H_5O(CH_2)_5CO_2H$	73[b]
IV		65	240 h	H^+	$C_6H_5O(CH_2)_4CH_3$	100[a]
V	$C_6H_5O(CH_2)_6Br$	20	15 min	H^+	$C_6H_5O(CH_2)_5CH_3$	100[a]
V		65	1 h	H^+	$C_6H_5O(CH_2)_5CH_3$	100[a]
V		65	1 h	CO_2	$C_6H_5O(CH_2)_6CO_2H$	80[b]

[a] GC yield of hydrolyzed product. [b] Isolated after reaction with substrate.

I with Mg* at −78 °C. The flask, containing Mg* (19.56 mmol) in 20 mL of THF, was cooled to −78 °C. I (1.58 mL, 9.83 mmol) was added via syringe over a 15-min period. The vessel was stirred 1 h, and then a 1-mL aliquot was removed and quenched with dilute HCl. GC analysis showed I to be completely consumed. The septum was replaced by a gas inlet, the condenser connected to an oil bubbler, and the flask blanketted with a CO_2 atmosphere for 2.5 h while the cooling was maintained. The mixture was worked up as in the previous reaction. II (1.065 g, 71%) was isolated as white crystals: mp 61–62 °C (ethanol) (lit. mp 62–63 °C,[14] 64–65 °C[15]); NMR (CCl_4) δ 2.1 (quintet, 2 H), 2.5 (t, 2 H), 3.9 (t, 2 H), 6.9–7.2 (m, 5 H), 11.65 (s, 1 H, C(O)OH); IR (KBr) 3500–3000 br cm^{-1}, 2940, 1690, 1235.

III with Mg*. III (1.6188 g, 7.07 mmol) was placed in a cone-bottomed test tube capped with a septum and then purged with argon for 30 min. Then 5 mL of THF was added. The solution was taken up into a syringe and added over a 15-min period to a slurry of Mg* (14.77 mmol) in 20 mL of THF. The vessel warmed slightly. The conical tube and syringe were rinsed with 2.5 mL of THF, which was added to the reaction vessel. After being stirred for an additional 15 min, the mixture was cannulated through an N_2-filled glovebag into a beaker of freshly crushed CO_2. The reaction was worked up as previously described to give 5-phenoxypentanoic acid (177.5 mg, 89%) as white crystals: mp 63–64 °C, (lit.[16] mp 65–66 °C); NMR (Unisolve-d) δ 1.5–2.0 (m, 4 H), 2.3 (t, 2 H), 3.9 (t, 2 H), 6.68–7.3 (m, 5 H); IR (KBr) 3500–2980 br cm^{-1}, 1710, 1235.

IV with Mg*. IV (1.1141 g, 4.58 mmol) was added dropwise over an 8-min period to a slurry of Mg* (14.8 mmol) in 20 mL of THF. The reaction was stirred an additional 15 min then worked up as III. 6-Phenoxyhexanoic acid (677.3 mg, 73%) was isolated as white crystals: mp 70.2–71 °C (lit.[17] mp 71 °C); NMR (Unisolve-d) δ 1.3–2 (m, 6 H), 2.2 (t, 2 H), 3.9 (t, 2 H), 6.7–7.3 (m, 5 H); IR (KBr) 3300–3000 cm^{-1}, 1710, 1240.

A second reaction employing Mg* (15.44 mmol) in 20 mL of refluxing THF was run in an effort to induce cyclization. IV (871.95 mg, 3.586 mmol) was added over an 8-min period. Quenches at 15 min, 1 h, and 24 h showed only hydrolyzed Grignard reagent. No phenol, cyclopentane, or pentene was observed by GC. After 240 h of reflux, the whole pot was quenched. Again, GC analysis showed only 1-phenoxypentane. It is possible that a small amount of cyclopentane or pentene would have been lost during the reflux period due to their volatility, but not phenol.

V with Mg*. V (1.6486 g, 6.41 mmol) was added dropwise over a 7-min period to Mg* (24.3 mmol) in 30 mL of THF. An aliquot at 15 min showed V to be consumed but no evidence of phenol or cyclohexane. A single new peak, presumably the hydrolyzed Grignard reagent, had appeared. The reaction was refluxed to try and induce cyclization, but the 1-h quench showed no change. The reaction was cannulated onto freshly crushed CO_2 and worked up as previously. 7-Phenoxyheptanoic acid (1.06125 g, 80%) was isolated as white crystals: mp 56.8–57.8 °C (lit.[18] mp 55 °C); NMR (Unisolve-d) δ 1.2–1.85 (m, 8 H), 2.25 (t, 2 H), 3.9 (t, 2 H), 6.7–7.3 (m, 5 H); IR (KBr) 3300–2900 cm^{-1}, 1705, 1245.

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Registry No. I, 588-63-6; II, 6303-58-8; III, 1200-03-9; IV, 22921-72-8; V, 51795-97-2; Mg, 7439-95-4; C_6H_5OH, 108-95-2; $C_6H_5O(CH_2)_4CO_2H$, 7170-40-3; $C_6H_5O(CH_2)_5CO_2H$, 7170-41-4; $C_6H_5O(CH_2)_4CH_3$, 2050-04-6; $C_6H_5O(CH_2)_5CH_3$, 1132-66-7; $C_6H_5O(CH_2)_6CO_2H$, 7170-42-5.

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A Homo-Brook Rearrangement

Stephen R. Wilson*[1] and Gregory M. Georgiadis

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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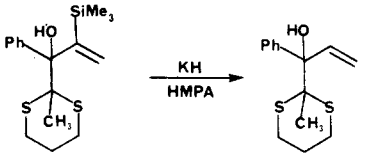
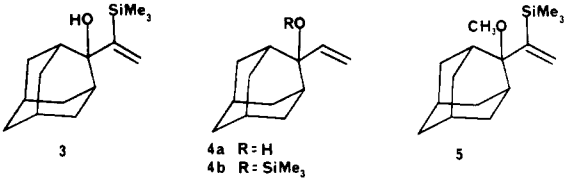
In the course of studying a series of anion-assisted rearrangements[2] (eq 1), we had occasion to react **1** with KH and HMPA. To our surprise, a rapid desilylation of **1** → **2** was observed.



1 2 (1)

The cleavage of unactivated carbon–silicon bonds was unusual,[3] and desilylation had not been observed in attempts to form allenes[4] via Peterson olefination.[5] We thus decided to examine the simpler system **3**.



3 4a R = H; 4b R = SiMe3 5

1-(Trimethylsilyl)vinyllithium[2] reacts with 2-adamantanone to produce alcohol **3** in 67% yield. When

(1) Address correspondence to this author at the Department of Chemistry, New York University, Washington Square, New York, NY 10003.
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(4) Compounds such as **1** and **3** were found to be "exceptionally resistant[7a] to elimination" under conventional Peterson[5] elimination conditions (NaH/THF).
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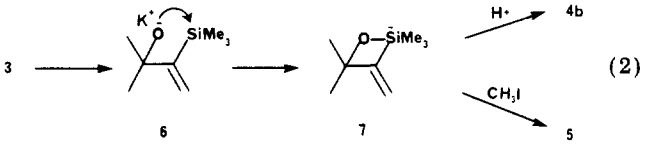
0022-3263/83/1948-4143$01.50/0

3 was treated with KH/THF, rapid migration[9] of the trimethylsilyl group from carbon to oxygen resulted with the formation of **4b**. The same reaction proceeded with HMPA as the solvent to form **4b** within 1 min at 0 °C. Isolation of product resulted in loss of trimethylsilyl to yield **4a**. If the reaction mixture is quenched with D_2O, no deuterium incorporation is observed at the vinyl carbon, but if the reaction is allowed to proceed *in the presence* of excess CH_3I, methyl ether **5** is formed.

We suggest the following mechanism:[6,7] deprotonation of 3 (eq 2) leads to highly basic alkoxide **6**, which may exist



(2)

as the pentavalent silicon anion **7**. Alkylation on oxygen or protonation on carbon leads to the observed products. In conclusion, the evidence[8] suggests that the Brook rearrangement may be more general than originally proposed.[9]

Experimental Section

Preparation of Compound 3. To a solution of 1 g (5.59 mmol) of α-bromovinyltrimethylsilane in 20 mL of dry ether at −78 °C was added 1.5 equiv of *tert*-butyllithium (Alfa). The mixture was warmed to −20 °C for 2 h, and then 825 mg (5.5 mmol) of 2-adamantanone in 10 mL of ether was added. After 1 h, the reaction was warmed to room temperature and worked up in the usual way to product 1.3 g of white crystals, mp 76–79 °C (95%). Recrystallization gave 923 mg, mp 84–85 °C (67%): TLC (silica gel, 5% ether/pentane) R_f 0.37; NMR (CCl_4) δ 4.5 (2 H, dd) 1.0–2.2 (14 H, m), 0.0 (9 H, s); IR (CCl_4) 3600 cm^{-1}; MS, *m/e* (relative intensity) 250 (1), 236 (27), 235 (90), 161 (36), 160 (100), 151 (85), 150 (78), 127 (19); calcd for $C_{15}H_{26}OSi$ 250.17529, found 250.17314.

Isomerization of Compound 3. A. A solution of 76 mg (0.3 mmol) of compound 3 in 0.5 mL of THF and 2 mL of HMPA was cooled to 0 °C and treated with a slight excess of KH (22% dispersion in oil). After 1 min, analysis (aliquot worked up with pentane/H_2O) revealed no starting material remaining, and GC, GC/MS, and TLC indicated mostly **4b** present. Usual workup (ether/H_2O) gave an oil, which was purified by preparative TLC to yield 20 mg of white crystals of **4a** (37%).[10] Compound **4a** possessed spectral and analytical properties identical with those of an authentic sample prepared by the addition of vinylmagnesium bromide to 2-adamantanone: TLC (5% ether/pentane) R_f 0.05; NMR δ 6.0–6.5 (m, 1 H), 4.9–5.4 (m, 2 H), 1.4–2.4 (m, 14 H), 1.1 (s, 1 H); IR (CCl_4) 3600 cm^{-1}.

B. A solution of 111 mg (0.44 mmol) of compound 3 in 5 mL of dry THF under argon was treated with a slight excess of KH (ca. 20% dispersion in oil, Alfa). The mixture was stirred at 0 °C for 5 min and then at room temperature for 1 h. Usual workup (ether/H_2O) gave an oil, which was purified by preparative TLC to yield 69 mg (63%) of compound **4b**: TLC (5% ether, pentane) R_f 0.57; NMR δ 5.6–6.1 (m, 1 H), 5.0–5.4 (m, 2 H), 1.2–2.4 (m, 14 H), 0.0 (s, 9 H); IR, no OH; MS, *m/e* (relative intensity) 250 (100), 235 (61), 181 (23), 161 (53), 91 (26), 79 (27), 75 (69), 73 (96); calcd for $C_{15}H_{26}OSi$ 250.17529, found 250.17438.

If the reaction mixture in method A or B was quenched with D_2O, no deuterium incorporation at the vinyl position was observed.

Alkylation of Anion 6. Alcohol 3 (76 mg, 0.3 mmol), a few (excess) milliliters of CH_3I (filtered through silica gel), and 5 mL of dry THF were cooled to 0 °C, and a slight excess of KH was added. After 10 min, GC analysis showed the disappearance of starting material. Usual workup gave 55 mg (73%) of compound **5** after preparative TLC: TLC (5% ether/pentane) R_f 0.62; NMR δ 5.6–5.7 (m, 2 H), 2.78 (s, 3 H), 1.1–2.3 (m, 14 H), 0.0 (s, 9 H); IR, no OH; MS, *m/e* (relative intensity) 251 (44), 250 (95), 235 (70), 207 (21), 193 (25), 181 (42), 168 (24), 165 (78), 161 (68), 160 (21), 119 (23), 117 (27), 105 (30), 91 (51), 89 (22), 81 (22), 79 (51), 77 (23), 75 (80), 73 (100), 67 (24); calcd for $C_{16}H_{28}OSi$ 264.19095, found 264.19073.

Registry No. 3, 66374-49-0; **4a**, 63563-16-6; **4b**, 87174-36-5; **5**, 87174-37-6; (α-bromovinyl)trimethylsilane, 13683-41-5; 2-adamantanone, 700-58-3.

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(8) A recent paper by Hudrlik reports other examples of the "Homo-Brook" rearrangement: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809–6811.

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(10) GC showed much of the silyl ether **4b** to be hydrolyzed *during workup* when HMPA was present. A small amount of **4b** was recovered from the preparative TLC of this experiment.

Dioxygenation and Reduction of 2′,3′-Unsaturated *C*-Nucleosides

Uli Hacksell and G. Doyle Daves, Jr.*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

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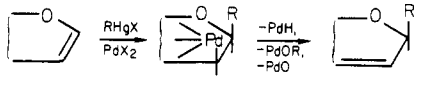
A large number of 2′,3′-unsaturated *N*-nucleosides[1] are synthetically available.[2] The regio- and stereospecific palladium-mediated reaction or organomercuric salts with furanoid or pyranoid glycals gives access also to a variety of 2′,3′-unsaturated *C*-nucleosides.[3,4] As part of a current exploration of the utility of these products as synthetic intermediates, we have dihydroxylated and reduced a few selected compounds with results that are noteworthy.



Catalytic cis dihydroxylation of 1[3e] (Scheme I) using osmium tetroxide and trimethylamine *N*-oxide[5] produced a mixture of two isomeric diols that could not be separated chromatographically. This mixture was treated with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid to afford the corresponding acetonide mixture (2 and 3), which was more amenable to chromatographic sepa-

(1) For convenience, we use the common carbohydrate numbering system (the anomeric carbon is designated 1′) in the running text. Correct nomenclature can be found in the Experimental Section.

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(4) The formation of 2′,3′-didehydro-2′,3′-dideoxy-1-methyl-5′-*O*-trityl-β-pseudouridine was recently reported as a byproduct in the synthesis of 2-deoxy-*C*-nucleosides: Matsuda, A.; Chu, C. K.; Reichman, U.; Pankiewicz, K.; Watanabe, K. A.; Fox, J. J. *J. Org. Chem.* **1981**, *46*, 3603.

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