New Applications of 1,5-Hydrogen Atom Transfer Reactions: Self-Oxidizing Protecting Groups

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Three new alcohol protecting groups are introduced: *o*-bromobenzyl, *o*-bromo(methylenedioxy)benzyl, and *o*-bromotrityl. Removal of these protecting groups under reductive conditions with tributyltin hydride is coupled with an oxidation of the substrate to produce directly an aldehyde or ketone. This oxidation occurs by 1,5-hydrogen transfer, followed by β-fragmentation. For example, treatment of the *o*-bromobenzyl ether of 3-phenyl-1-propanol with tibutyltin hydride at 0.001 M (80 °C) directly produces 3-phenyl-1-propanal. An application to the selective oxidation of primary alcohols in the presence of secondary alcohols is also introduced.

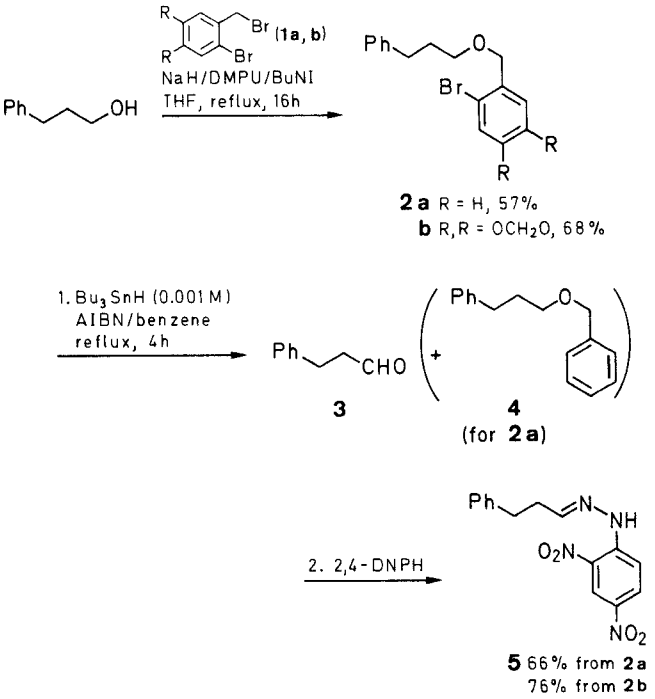
The protection of functional groups[2] and the interconversion of functional groups by reduction or oxidation are two fundamental synthetic tactics that are rarely coupled. A sequence of protection and deprotection almost always leaves a functional group in the same oxidation state after deprotection as before. However, it is not uncommon to carry a functional group through a synthetic sequence in a different oxidation state from that which is ultimately required. For example, aldehydes and ketones are often carried as protected alcohols. To convert the protected functional groups to the required end products, two steps – deprotection and oxidation (or reduction) – are usually required. It would be desirable to have a suite of protecting groups which, when removed, directly formed products in a higher (or lower) oxidation state than the precursors.

We now introduce the first members of a new class of protecting groups. These protecting groups are installed at the alcohol oxidation state. Their removal under mild conditions is coupled with an oxidation of the substrate to an aldehyde or ketone, hence the name "self-oxidizing protecting groups". This class of reagents also has use beyond the field of protecting group chemistry for conducting selective oxidations. Most significantly, the oxidations occur under conditions that are traditionally considered as mildly reductive (Bu_3SnH), and thus the chemo- and regioselectivities observed are completely unrelated to the ease of oxidation of the functional groups in a given substrate.

The basic concept is outlined in Scheme 1. 3-Phenyl-1-propanol is "protected" by *O*-alkylation with *o*-bromobenzyl bromide (**1a**).[3] The resulting *o*-bromobenzyl ether **2a** is a variant of a standard benzyl ether, and we have previously used this modified benzyl ether to conduct sequences of radical translocation/cyclization.[4] In the case at hand, direct "deprotection" of **2a** was accomplished by reduction with tributyltin hydride at 0.001 M. This formed 3-phenylpropanal (**3**) and the benzyl ether **4** in a ratio of about 5:1. The 2,4-dinitrophenyl hydrazone derivative **5**[5] of 3-phenylpropanal was isolated in 66% yield.

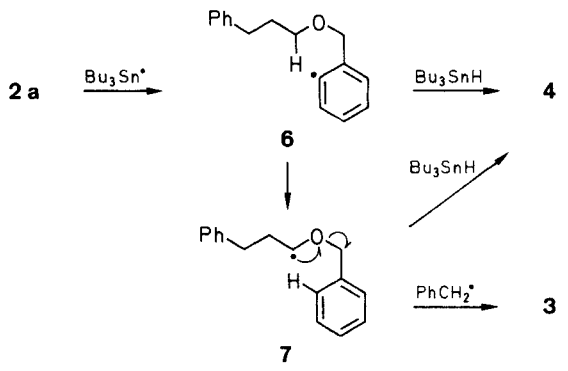
A probable sequence for formation of **3** is readily formulated, as outlined in Scheme 2. Initial bromine abstraction is followed by 1,5-hydrogen transfer[6] from aryl radical **6** to give α-alkoxy radical **7**. Fragmentation[7] of **7** gives aldehyde **3** and the benzyl radical, which presumably abstracts hydrogen from tributyltin hydride[8] to form toluene and continue the chain. Each of these steps is a well-known radical reaction. The combination couples the removal of the *o*-bromobenzyl protecting group with oxidation of the substrate from an alcohol to an aldehyde. The use of low tin hydride concentrations is critical since trapping of either radical **6** or radical **7** by hydrogen transfer derails the sequence by forming **4**.

We have conducted a similar sequence of reactions starting with the methylenedioxy analog **2b** (Scheme 1),

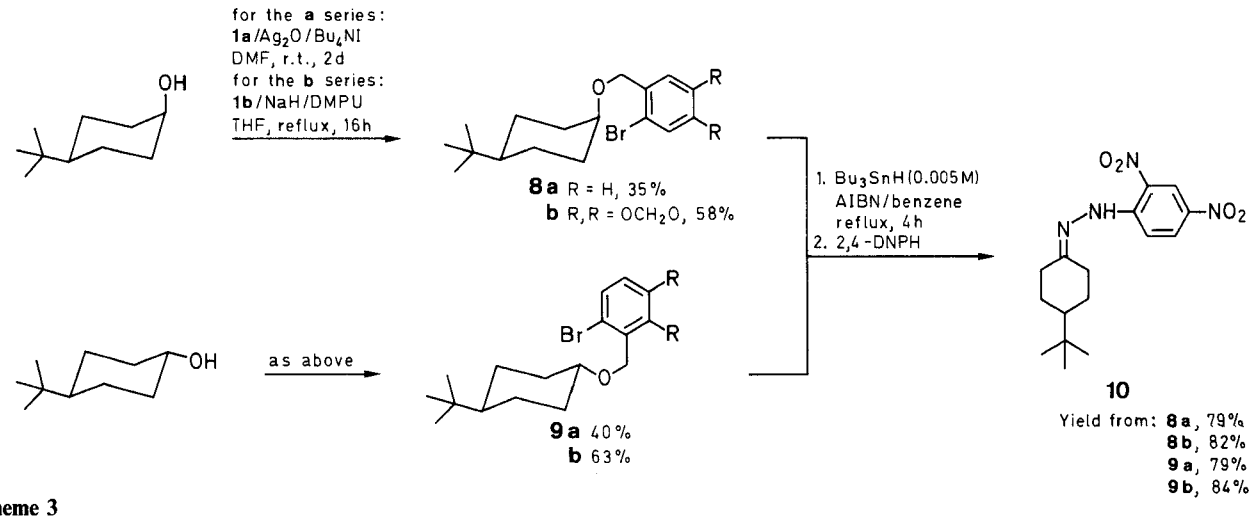


DMPU = 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone

Scheme 1



Scheme 2

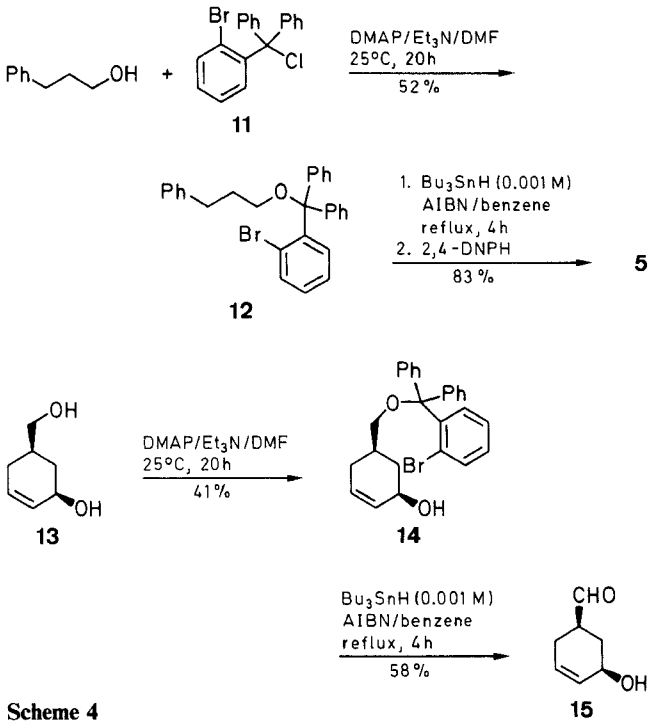


Scheme 3

and slightly better yields of **5** are obtained in the deprotection step. However, the *o*-bromo(methylenedioxy)benzyl bromide is a more reactive alkylating agent, and better yields are also obtained in the protection step.[9] The yield differences in the protection step are even larger for secondary alcohols, as shown in Scheme 3. Both *cis*- and *trans*-4-tert-butylcyclohexanol were "protected" with **1a** and **1b**, and then "deprotected" to give the dinitrophenyl hydrazone derivative **10**. Protection steps proceeded with better efficiency in the **b** series, but deprotection yields were all comparable. Only traces of the directly reduced benzyl ethers were formed when the tin hydride reduction was conducted at 0.005 M. Taken together with the previous results, this means that most of the reduced, debrominated products in Scheme 2 probably resulted from failed 1,5-hydrogen transfer (**6** → **7**) and not failed fragmentation (**7** → **3**).[10]

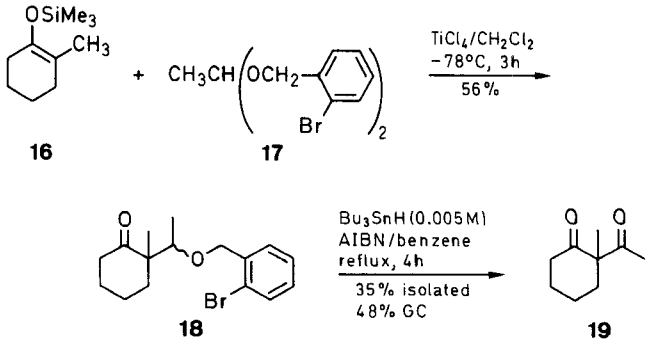
We envision that these protecting groups and others like them can be useful in complex synthesis. Only the functionality bearing the protecting group is targeted for oxidation, and even that oxidation is accomplished under reductive conditions. This analysis suggests a second application of such groups for selective oxidation. The ability to selectively oxidize a given alcohol in a polyol would be determined by its ease of derivatization rather than its ease of oxidation.

To implement this idea, we prepared *o*-bromotrityl chloride (**11**)[11] as a variant of the standard trityl protecting group (Scheme 4). Tritylation[12] of 3-phenyl-1-propanol gave **12** in 52% yield. Reduction of **12** with tin hydride and subsequent hydrazone formation produced DNP derivative **5** in 83% yield. Next, we demonstrated the possibilities for selective oxidation of a diol. As expected, tritylation with **11** was selective for the primary hydroxy group, and only monotrityl derivative **14** was formed from **13**. Reduction of **14** with tin hydride produced the sensitive[13] hydroxy aldehyde **15** in 58% yield. Overall, a selective oxidation of a primary hydroxy group in the presence of an unprotected secondary allylic hydroxy group was accomplished. This very difficult transformation is usually orchestrated by juggling different protecting groups on primary and secondary alcohols.[14]



Scheme 4

Another variant on the theme couples the introduction of the protecting group with a standard C–C bond forming reaction. Scheme 5 illustrates this concept by using the Mukaiyama aldol reaction[15] of **16** with **17** to give **18** as a mixture of diastereomers. Reduction of **18**



Scheme 5

with tin hydride was not an especially clean reaction, but we were able to isolate **19**[16] in 35% yield. The GC yield of **19** was 48%.

These simple examples suffice to illustrate that self-oxidizing protecting groups should facilitate the execution of complex synthetic sequences in many different ways. We have introduced three such groups (*o*-bromobenzyl, *o*-bromo(methylenedioxy)benzyl, and *o*-bromotrityl), and it should certainly be possible to develop new members of the class. However, we caution that the scope of these reactions is not yet well established. As yet, we have made no effort to optimize conditions in either the protection or deprotection steps. Further, relatively little is known about substituent effects on 1,5-hydrogen transfer reactions from C–H bonds to carbon-centered radicals, and this is an especially vulnerable step. Fragmentation reactions of α-alkoxyalkyl radicals have also not been studied in complex systems. For the moment, we recommend that appropriate model studies should precede the attempted application of these or related groups in complex synthetic problems.

1-(2′-Bromophenyl)-5-phenyl-2-oxapentane (2a):
A solution of DMPU (4.40 mmol, 0.5 mL), 60% NaH (4.40 mmol, 176 mg) and 3-phenyl-1-propanol (3.67 mmol, 500 mg) in THF (40 mL) was refluxed for 0.5 h. After cooling to 0 °C, 2-bromobenzyl bromide (3.74 mmol, 0.58 mL) and Bu_4NI (0.37 mmol, 136 mg) were added, and the mixture refluxed for 16 h. The turbid solution was filtered, diluted with Et_2O (100 mL), washed with water and brine, dried ($MgSO_4$), and concentrated. The crude product was isolated by flash column chromatography (EtOAc/hexane = 1:30) to give **2a** (57%, 638 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.14 (9H, m), 4.56 (2H, s), 3.57 (2H, t, J = 6.3 Hz), 2.75 (2H, t, J = 7.4 Hz), 1.98 (2H, quint., J = 6.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.92, 137.94, 132.47, 128.89, 128.82, 128.53, 128.39, 127.37, 125.81, 122.64, 72.14, 70.00, 32.41, 31.38.

IR (neat): ν = 3026, 2939, 2860, 1105, 1124 cm^{-1}.

MS: m/z = 306 (M + 2), 304 (M), 288, 245, 207, 185, 169, 118, 91 (base peak).

HRMS for $C_{16}H_{17}BrO$ calcd 304.0463, found 304.0463.

1-(6′-Bromopiperonyl)-5-phenyl-2-oxapentane (2b):
Compound **2b** was prepared following the procedure for **2a** with DMPU (2.64 mmol, 0.32 mL), 60% NaH (2.64 mmol, 106 mg), 3-phenyl-1-propanol (2.2 mol, 300 mg), 6-bromopiperonyl bromide (2.64 mmol, 777 mg), and Bu_4NI (0.22 mmol, 81 mg) in THF (20 mL). Purification by flash column chromatography (EtOAc/hexane = 1:5) gave **2b** (68%, 522 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–6.99 (7H, m), 5.98 (2H, s), 4.67 (2H, s), 3.54 (2H, t, J = 6.3 Hz), 2.74 (2H, t, J = 7.5 Hz), 1.96 (2H, quint., J = 6.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.64, 147.50, 141.98, 131.27, 128.56, 128.40, 125.85, 113.13, 112.61, 109,20, 101.74, 72.05, 69.88, 32.47, 31.41.

IR (neat): ν = 2862, 1477, 1244, 1113 cm^{-1}.

MS: m/z = 350 (M + 2), 348 (M), 229, 215 (base peak) 157, 135, 117, 105, 91, 77.

HRMS for $C_{17}H_{17}BrO_3$ calcd 348.0361, found 348.0361.

3-Phenylpropanal 2′,4′-Dinitrophenylhydrazone (5):
A solution of **2a** or **2b** (0.252 mmol), Bu_3SnH (0.302 mmol, 81 μL) and AIBN (0.025 mmol, 4.2 mg) in benzene (0.001 M, 252 mL) was refluxed for 4 h under N_2. The crude mixture was treated with I_2/DBU,[17] filtered through a pad of silica gel, and concentrated. The crude product was reacted with a solution of 2,4-dinitrophenylhydrazine, filtered and washed with MeOH to give the product **5** (66% from **2a**, 76% from **2b** and 83% from **12**) as a yellow solid (mp 146–148 °C).

^1H NMR (300 MHz, $CDCl_3$): δ = 11.19 (1H, s), 9.10 (1H, d, J = 2.4 Hz), 8.29 (1H, dd, J = 2.4, 7.0 Hz), 7.92 (1H, d, J = 7.3 Hz), 7.55 (1H, t, J = 5.0 Hz), 7.35–7.23 (5H, m), 2.97 (2H, t, J = 7.1 Hz), 2.79 (2H, quint., J = 5.2 Hz).

IR ($CHCl_3$): ν = 3312, 3030, 1651, 1556, 1506, 1385, 1196 cm^{-1}.

***cis*-(2′-Bromobenzyloxy)-4-*tert*-butylcyclohexane (8a):**
A solution of *cis*-4-*tert*-butylcyclohexanol (3.20 mmol, 500 mg), 2-bromobenzyl bromide (4.8 mmol, 0.75 mL), Ag_2O (9.6 mmol, 2.22 g), and Bu_4NI (0.32 mmol, 20 mg) in DMF (15 mL) was stirred for 2 days under N_2. The crude mixture was filtered through a pad of Celite, diluted with Et_2O (50 mL), washed with brine and water, dried ($MgSO_4$), and concentrated. The crude product was isolated by flash column chromatography (EtOAc/hexane = 1:40) to give **8a** (35%, 364 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.06–7.12 (4H, m), 4.55 (2H, s), 3.69 (1H, br s), 2.08 (2H, m), 1.60–0.97 (5H, m), 0.87 (9H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.91, 132.31, 128.75, 128.49, 127.40, 122.31, 73.36, 69.03, 48.04, 32.67, 30.65, 27.62, 21.61.

IR (neat): ν = 2941, 2864, 1441, 1365, 1089, 1026 cm^{-1}.

***cis*-(6′-Bromopiperonyloxy)-4-*tert*-butylcyclohexane (8b):**
Compound **8b** was prepared following the procedure for **2a** with DMPU (3.23 mmol, 0.39 mL), 60% NaH (5.38 mmol, 215 mg), *cis*-4-*tert*-butylcyclohexanol (2.69 mmol, 420 mg), 6-bromopiperonyl bromide (2.69 mmol, 790 mg), and Bu_4NI (0.269 mmol, 99 mg) in THF (30 mL). Purification by flash column chromatography (EtOAc/hexane = 1:5) gave **8b** (58%, 576 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.05 (1H, s), 6.97 (1H, s), 5.96 (2H, s), 4.24 (2H, s), 3.65 (1H, s), 2.12–1.97 (2H, m), 1.58–0.98 (7H, m), 0.86 (9H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.32, 132.51, 112.54, 112.45, 108.99, 101.64, 73.18, 68.91, 48.04, 32.64, 30.60, 27.60, 21.61.

IR (neat): ν = 2942, 2830, 1558, 1541, 1260, 1041 cm^{-1}.

MS: m/z = 370 (M + 2), 368 (M), 215, 213, 151, 135, 105, 78, 57 (base peak).

HRMS for $C_{18}H_{25}B_rO_3$ calcd 368.0987, found 368.0987.

***trans*-(2′-Bromobenzyloxy)-4-*tert*-butylcyclohexane (9a):**
Compound **9a** was prepared following the procedure for **8a** with *trans*-4-*tert*-butylcyclohexanol (1.28 mmol, 200 mg), 2-bromobenzyl bromide (1.54 mmol, 0.24 mL), Ag_2O (3.84 mmol, 890 mg), and Bu_4NI (0.128 mmol, 47 mg) in DMF (5 mL). Purification by flash column chromatography (EtOAc/hexane = 1:30) gave **9a** (40% 166 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.08 (4H, m), 4.60 (2H, s), 3.30 (1H, m), 2.19–2.15 (2H, m), 1.83–1.60 (2H, m), 1.30–0.97 (5H, m), 0.85 (9H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.59, 133.96, 132.60, 129.08, 127.97, 122.64, 78.81, 69.36, 47.49, 47.32, 36.10, 32.80, 27.72, 25.68.

IR (neat): ν = 2945, 2862, 1095, 1026 cm^{-1}.

MS: m/z 326 (M + 2), 324 (M), 267, 249, 227, 225, 171, 169 (base peak), 138, 57.

HRMS for $C_{17}H_{25}BrO$ calcd 324.1089, found 324.1089.

***trans*-(6′-Bromopiperonyloxy)-4-*tert*-butylcyclohexane (9b):**
Compound **9b** was prepared following the procedure for **2a** with DMPU (2.76 mmol, 0.30 mL), 60% NaH (4.6 mmol, 184 mg), *trans*-4-*tert*-butylcyclohexanol (2.30 mmol, 360 mg), 6-bromopiperonyl bromide (2.30 mmol, 680 mg), and Bu_4NI (0.23 mmol, 85 mg) in THF (25 mL). Purification by flash column chromatography (EtOAc/hexane = 1:5) gave **9b** (63%, 536 mg) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.01 (1H, s), 6.98 (1H, s), 5.96 (2H, s), 4.51 (2H, s), 3.27 (1H, m), 2.18–2.10 (2H, m), 1.83–1.75 (2H, m), 1.36–0.94 (5H, m), 0.85 (9H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.46, 131.93, 112.93, 112.55, 109.25, 101.68, 78.55, 69.19, 47.49, 32.80, 32.38, 27.71, 25.69.

IR (neat): ν = 2950, 2830, 1558, 1541, 1109, 1041 cm^{-1}.

MS: *m/z* 370 (M + 2), 368 (M), 215, 213, 151, 135, 81, 76, 57 (base peak).

HRMS for $C_{18}H_{25}BrO_3$ calcd 368.0987, found 368.0987.

4-*tert*-Butylcyclohexanone 2',4'-Dinitrophenylhydrazone (10):
Compound **10** was prepared following the procedure for **5** with the appropriate precursor (**8a**, **8b**, **9a**, or **9b**, 0.276 mmol), Bu_3SnH (0.331 mmol, 89 µL), and AIBN (0.027 mmol, 4.4 mg) in benzene (0.005 M, 55 mL) to give the product **10** (73% from **8a**, 82% from **8b**, 79% from **9a**, and 89% from **9b**) as a yellow solid (mp 151–152°C).

^1H NMR (300 MHz, $CDCl_3$): δ = 11.20 (1 H, s), 9.12 (1 H, d, *J* = 2.6 Hz), 8.29 (1 H, dd, *J* = 2.6, 7.1 Hz), 7.97 (1 H, d, *J* = 9.6 Hz), 2.98–1.22 (9 H, m), 0.92 (9 H, s).

IR ($CHCl_3$): ν = 3397, 3030, 2922, 2729, 1651, 1556, 1567, 1385, 1261 cm^{-1}.

1-(2'-Bromophenyl)-1,1,5-triphenyl-2-oxapentane (12).
A solution of *o*-bromotrityl chloride (1.03 mmol, 370 mg) and 3-phenyl-1-propanol (0.734 mmol 0.10 mL) in DMF (10 mL) was cooled to 0°C and added to Et_3N (2.20 mmol, 0.27 mL) and DMAP (0.073 mmol, 9 mg), and allowed to warm to 25°C. After 20 h at 25°C, the mixture was diluted with Et_2O (50 mL), washed with aq NH_4Cl and brine, dried ($MgSO_4$), and concentrated. Flash column chromatography (EtOAc/hexane = 1:10) of the residue gave **12** (52%, 174 mg) as a pale green oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.01 (19 H, m), 3.11 (2 H, t, *J* = 6.4 Hz), 2.73 (2 H, t, *J* = 7.3 Hz), 1.98 (2 H, quint., *J* = 6.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.70, 142.06, 135.62, 128.98, 128.69, 128.42, 128.27, 127.72, 127.63, 126.76, 126.68, 124.23, 86.86, 63.54, 32.58, 31.72.

IR (neat): ν = 3061, 3026, 2938, 1495, 1448, 1215, 1161, 1072 cm^{-1}.

MS: *m/z* 458 (M + 2), 456 (M) 381, 379, 339, 337, 323, 241, 183, 119, 105, 91 (base peak), 77, 65, 51.

HRMS for $C_{28}H_{25}BrO$ calcd 456.1089, found 456.1089.

(1*R,5*R**)-5-[2'-Bromophenyl(diphenyl)methyloxymethyl]-2-cyclohexen-1-ol (14):**
Compound **14** was prepared following the procedure for **12** with *o*-bromotrityl chloride (2.184 mmol, 781 mg), (1*R**, 5*R**)-5-(hydroxymethyl)-2-cyclohexen-1-ol (1.56 mmol, 200 mg), Et_3N (4.68 mmol, 0.57 mL), and DMAP (0.156 mmol, 19 mg) in DMF (10 mL). Purification by flash column chromatography (EtOAc/hexane = 1:1) gave **14** (41%, 287 mg) as a yellow solid (mp 55–56°C).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.05 (14 H, m), 5.88–5.62 (2 H, m), 4.36 (1 H, br s), 2.98 (2 H, d, *J* = 5.9 Hz), 2.35–1.15 (6 H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.83, 141.85, 135.74, 131.66, 129.18, 128.46, 128.33, 127.62, 126.81, 126.75, 86.63, 68.29, 67.97, 36.49, 34.00, 28.92.

IR ($CHCl_3$): ν = 3082, 3049, 2945, 2882, 1681, 1070, 1026 cm^{-1}.

MS: *m/z* = 450 (M + 2), 448 (M), 432, 399, 371, 369, 339, 337, 323, 321, 242, 183, 165, 105, 97 (base peak), 93, 67, 55.

HRMS for $C_{26}H_{23}BrO$ (M–H_2O) calcd 430.0932, found 430.0932.

(1*R*,*,5*R)-5-Hydroxy-3-cyclohexene-1-carboxaldehyde (15):**
Compound **15** was prepared following the procedure for **5** with **14** (0.207 mmol, 93 mg), Bu_3SnH (0.248 mmol, 67 µL), and AIBN (0.025 mmol, 3.4 mg) in benzene (207 mL). The crude sample was rather pure: ^1H NMR (300 MHz, $CDCl_3$): δ = 9.70 (1 H, s), 5.78 (2 H, br s), 4.26 (1 H, br s), 2.75–0.85 (6 H, m). Purification by flash column chromatography (EtOAc/hexane = 1:1) gave a mixture of **15** and other isomers (believed to be lactols and an epimer[14]) as a colorless oil (58%, 15 mg).

^1H NMR (300 MHz, $CDCl_3$): δ = 9.76–9.63 (1 H, m), 6.12–5.53 (2 H, m), 4.65–4.18 (1 H, m), 2.79–0.84 (6 H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.16, 203.45, 131.46, 130.76, 128.72, 127.59, 127.30, 126.78, 103.15, 72.40, 65.08, 62.76, 44.83, 42.15, 41.06, 31.30, 24.39, 23.76.

IR (neat): ν = 3397, 3030, 2922, 2729, 1716, 1651, 1051 cm^{-1}.

MS: *m/z* = 125 (M), 111, 108, 97, 79 (base peak), 69, 55.

HRMS for $C_7H_{10}O_2$ calcd 126.0681, found 126.0681.

2-[1-(2'-Bromobenzyloxy)ethyl]-2-methylcyclohexanone (18):
To a solution of 2-methyl-1-trimethylsiloxycyclohexane (7.37 mmol, 1.36 g) and bis(2-bromobenzyl)acetal (7.37 mmol, 2.95 g) in CH_2Cl_2 (100 mL) at −78°C under N_2 was added $TiCl_4$ (8.84 mmol, 9 mL of 1.0 M in CH_2Cl_2 solution). After stirring 3 h at −78°C, the mixture was quenched with water (2 mL), extracted with Et_2O (50 mL × 3), washed with aq $NaHCO_3$, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (EtOAc/hexane = 1:5) gave **18** (56%, 1.34 g, 1/1 mixture of diastereomers) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.08 (4 H, m), 4.72–4.35 (2 H, m), 4.16–4.02 (1 H, m), 2.67–1.33 (8 H, m), 1.47–1.28 (6 H, m).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.45, 214.08, 138.22, 137.93, 132.12, 131.95, 128.72, 128.48, 127.31, 127.16, 122.18, 121.81, 77.71, 76.29, 70.40, 69.77, 53.33, 39.42, 38.76, 35.92, 33.68, 27.36, 26.44, 20.77, 20.60, 18.74, 18.28, 13.30.

IR (neat): ν = 3030, 2922, 1716, 1196, 1051 cm^{-1}.

MS: *m/z* = 326 (M + 2), 324 (M), 282, 280, 215, 213, 171, 169 (base peak), 140, 90, 83.

HRMS for $C_{14}H_{19}BrO$ (M – CH_2CO) calcd 282.0619, found 282.0619.

2-Acetyl-2-methylcyclohexanone (19).
Compound **19** was prepared following the procedure for **5** with **18** (0.461 mmol, 150 mg), Bu_3SnH (0.532 mmol, 171 µL) and AIBN (0.046 mmol, 7.57 mg) in benzene (93 mL). Purification by flash column chromatography (EtOAc/hexane = 1:10) gave **19** (29 mg, 35% isolated, 48% GC) as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.55–2.27 (3 H, m), 2.12 (3 H, s), 2.03–1.39 (5 H, m), 1.24 (3 H, s).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.90, 207.78, 63.38, 40.81, 36.43, 26.93, 25.28, 21.99, 20.40.

IR (neat): ν = 2922, 1714, 1651, 1435.

MS: *m/z* 154 (M), 139, 126, 112 (base peak), 97, 84, 69, 59, 55, 43.

HRMS for $C_9H_{14}O_2$ calcd 154.0994, found 154.0994.

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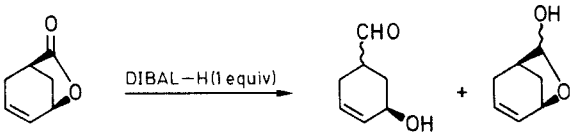

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