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A CONVENIENT ONE-FLASK PROCEDURE FOR THE DIRECT CONVERSION OF ALKENES TO HOMOALLYLIC ALCOHOLS

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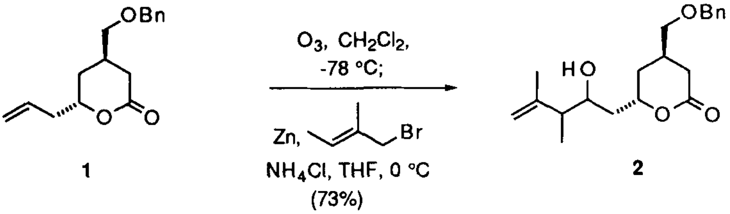
Abstract: Homoallylic alcohols have been prepared from alkenes by direct reaction of the ozonide with an allylic bromide in the presence of zinc.

During the early stages of a projected total synthesis of the neoclerodane diterpenoid insect antifeedant jodrellin B,[1] the need arose to effect the conversion of **1** into **2**. The challenge associated with achieving this objective was quickly made apparent when the aldehyde produced through ozonolytic cleavage of **1** proved to be extremely sensitive to purification and/or further chemical processing. We report herein a simple procedure for accomplishing such a transformation that relies on the



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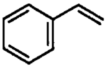
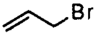
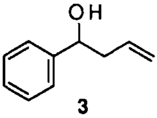
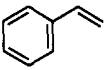
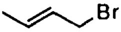
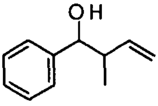
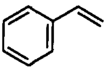
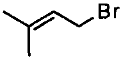
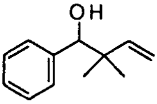
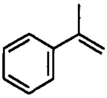
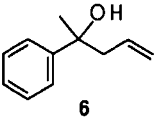
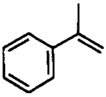
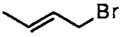
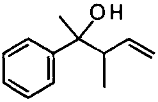
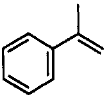
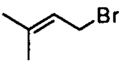
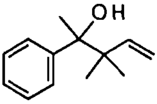
concept of *in situ* reduction of the ozonide in the midst of an allylzinc reagent. The importance of homoallylic alcohols as synthetic intermediates is widely recognized. Their availability in a total elapsed time of less than one hour at the 5 mmol level provides an unprecedented convenience factor. One's ability to skirt any handling of an aldehyde in a one-pot laboratory operation is another attractive feature of the present methodology.

Table 1.

alkene	allyl bromide	product	yield, %
		 **3**	87
		 **4**	60[a]
		 **5**	89
		 **6**	58
		 **7**	61[b]
		 **8**	71

[a] Syn/anti = 1.67:1.[2] [b] Syn/anti = 2.77:1.[3]

As shown in Table 1, the examples reported on herein make use of styrene and α-methylstyrene as the olefin reaction partner, with allyl, crotyl, and prenyl bromides as the co-reagents. The initial ozonolysis is best effected in dichloromethane at -78 °C. Since this solvent system is ineffective for coupling to the zinc reagent, exchange with tetrahydrofuran must precede the second stage of the process.

The intermediate ozonides are smoothly and rapidly transformed by powdered zinc into the corresponding aldehydes, which enter immediately into capture of the allylzinc species with customary allylic rearrangement. The synthetic utility of this process is highlighted by the conversion of **1** into **2** in 73% yield.

Representative Experimental Procedure: A solution of styrene (510 mg, 4.90 mmol) in CH_2Cl_2 (25 mL) was cooled to -78 °C, purged with a stream of oxygen for 10 min, and ozonolyzed until a persistent blue color was realized. The reaction mixture was purged with oxygen until colorless and concentrated under reduced pressure in the absence of heat. The residue was taken up in THF (25 mL), diluted with saturated NH_4Cl solution (5 mL), cooled to 0 °C, and treated with allyl bromide (1.02 mL, 11.8 mmol) followed by zinc dust (1.41 g, 21.5 mmol). After 15 min of stirring, ether and water were added, and the separated organic phase was washed with brine, dried, and concentrated. Purification over silica gel (elution with 10% ethyl acetate in hexanes) gave the homoallylic alcohol as a colorless oil (632 mg, 87%).

Data below correspond to the entries in Table 1.

1-Phenyl-3-buten-1-ol (3): ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.81 (m, 1H), 5.19-5.12 (m, 2H), 4.68 (t, J = 6.5 Hz, 1H), 2.83 (br s, 1H), 2.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 143.8, 134.3, 128.1, 127.2, 125.7, 117.8, 73.2, 43.5.

From reference 4: ^{1}H NMR ($CDCl_3$) δ 7.34 (m, 5H), 5.82 (m, 1H), 5.16 (m, 2H), 4.72 (t, *J* = 7 Hz, 1H), 2.50 (m, 2H), 2.15 (br s, 1H); ^{13}C NMR ($CDCl_3$) ppm 143.8, 134.4, 128.3, 127.4, 125.8, 118.2, 73.3, 43.7.

2-Methyl-1-phenyl-3-buten-1-ol (4): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28 (m, 5H), 5.81-5.64 (m, 1H), 5.21-4.96 (m, 2H), 4.56 (d, *J* = 5.5 Hz, 1H, syn), 4.32 (d, *J* = 7.9 Hz, 1H, anti), 2.63-2.39 (m, 1H), 2.04 (br s, 1H), 0.98 (d, *J* = 6.8 Hz, 3H, syn), 0.84 (d, *J* = 6.8 Hz, 3H, anti).

From reference 2: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35 (s, 5H), 6.1-5.6 (m, 1H), 5.7-5.0 (m, 2H), 4.66 (d, *J* = 5.0 Hz, 1H, syn), 4.43 (d, *J* = 8.5 Hz, 1H, anti) 2.7-2.25, (m, 1H), 2.60 (s, 1H), 1.01 (d, *J* = 6.8 Hz, 3H, syn), 0.87 (d, *J* = 7.0 Hz, 3H, anti).

2,2-Dimethyl-1-phenyl-3-buten-1-ol (5): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 5H), 5.87 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.12-4.98, (m, 2H), 4.36 (s, 1H), 2.08 (s, 1H), 0.97 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 145.0, 140.7, 127.7, 127.4, 127.3, 113.7, 80.5, 42.1, 24.4, 21.0.

From reference 5: ^{1}H NMR ($CDCl_3$) δ 7.33-7.24 (m, 5H), 5.91 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.13 (dd, *J* = 10.8, 1.5 Hz, 1H), 5.07, (dd, *J* = 17.6, 1.5 Hz, 1H), 4.41 (s, 1H), 2.07 (s, 1H), 1.01 (s, 3H), 0.95 (s, 3H); ^{13}C NMR ($CDCl_3$) ppm 145.0, 140.7, 127.7, 127.44, 127.38, 113.8, 80.6, 42.2, 24.4, 21.0.

1-Methyl-1-phenyl-3-buten-1-ol (6): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.36 (m, 2H), 7.26 (m, 1H), 5.67 (m, 1H), 5.18-5.11, (m, 2H), 2.70 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.53 (dd, *J* = 13.7, 8.1 Hz, 1H), 2.39 (br s, 1H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 147.5, 133.6, 128.0, 126.4, 124.7, 119.0, 73.5, 48.3, 29.6.

From reference 4: ^{1}H NMR ($CDCl_3$) δ 7.43 (m, 2H), 7.34 (m, 2H), 7.23 (m, 1H), 5.62 (m, 1H), 5.12, (m, 2H), 2.68 (dd, J = 14, 6 Hz, 1H), 2.50 (dd, J = 14, 8 Hz, 1H), 2.08 (s, 1H), 1.55 (s, 3H); ^{13}C NMR ($CDCl_3$) ppm 147.6, 133.6, 128.1, 126.6, 124.7, 119.3, 73.6, 48.4, 29.8.

1-Phenyl-1,2-dimethyl-3-buten-1-ol (7): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49-7.19 (m, 5H), 5.87-5.59 (m, 1H) 5.10-5.01 (m, 2H), 2.59-2.47 (m, 1H), 1.95 (br s, 1H), 1.57 (s, 3H, anti) 1.57 (s, 3H, syn), 0.93 (d, J = 6.9 Hz, anti), 0.83 (d, J = 6.9 Hz, 1H, syn).

From reference 3: Syn isomer: ^{1}H NMR ($CDCl_3$) δ 7.45-7.20 (m, 5H), 5.83 (d, J = 8.2 Hz, 1H) 5.14-5.08 (ddd, J = 1.8, 0.9, 0.6 Hz, 2H), 2.55 (m, 1H), 1.54 (s, 3H) 0.87 (d, J = 6.9 Hz, 3H).

Anti isomer: ^{1}H NMR ($CDCl_3$) δ 7.45-7.20 (m, 2H), 5.72 (d, J = 7.5 Hz, 1H) 5.14-5.08 (ddd, J = 1.8, 1.1, 0.8 Hz, 2H), 2.61 (m, 1H), 1.54 (s, 3H) 0.97 (d, J = 6.9 Hz, 3H).

1-Phenyl-1,2,2-trimethyl-3-buten-1-ol (8): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40-7.20 (m, 5H), 5.91 (dd, J = 17.4, 10.9 Hz, 1H), 5.07 (dd, J = 10.9, 1.5 Hz, 1H), 5.01 (dd, J = 17.4, 1.5 Hz, 1H), 1.90 (br s, 1H), 1.53 (s, 3H), 0.98 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) ppm 145.3, 145.1, 127.1, 127.0, 126.4, 113.7, 77.5, 44.3, 25.3, 22.7, 22.4.

From reference 6: ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.43-7.20 (m, 5H), 5.95 (dd, J = 17.5, 10.9 Hz, 1H), 5.13-5.02 (m, 2H), 1.94 (br s, 1H), 1.57 (s, 3H), 1.01 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) ppm 145.3, 145.1, 127.1, 127.0, 126.4, 113.8, 44.3, 25.3, 22.7, 22.4.

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