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Mono-Alkylation of Diols Through Ruthenium-Catalyzed Reaction with Homoallyl Alcohols

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SYNTHETIC COMMUNICATIONS, 28(3), 507-515 (1998)

MONO-ALKYLATION OF DIOLS THROUGH RUTHENIUM-CATALYZED REACTION WITH HOMOALLYL ALCOHOLS

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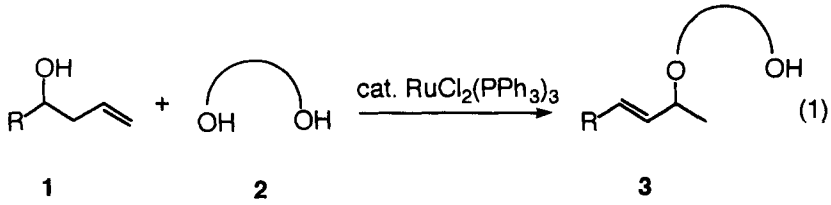
Abstract: Under the catalysis of $RuCl_2(PPh_3)_3$, a variety of diols reacted with homoallylic alcohols, generating mono-allyl ethers. Di-, tri-, and tetra-(ethylene glycols) all reacted to give mono ethers. Under the same conditions, primary hydroxyl groups reacted preferentially over secondary ones.

Mono-alkylated ethylene glycol oligomers are useful in the preparation of various crown ethers.[1] Recently, we reported that the functionalities of homoallylic alcohols were selectively repositioned under the catalysis of a ruthenium complex in water.[2] This process was explained as an olefin migration[3] followed by an allylic alcohol rearrangement.[4] Here we report the preparation of various mono-ethers from the reaction of homoallylic alcohols with various diols through the ruthenium catalyzed reaction (Eq. 1).



* To whom correspondence should be addressed.

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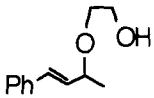
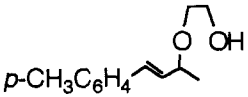
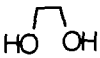
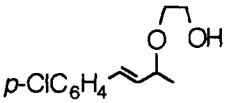
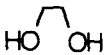
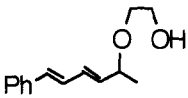
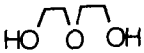
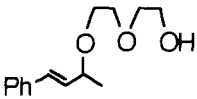
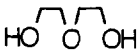
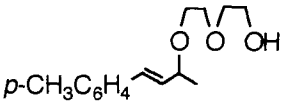
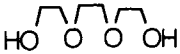
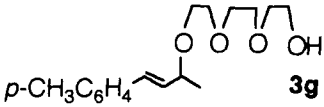
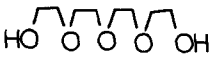
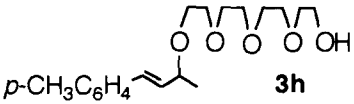
Table. Mono Alkylation of Diols Catalyzed by Ruthenium

Entry	R- (1)	Diol (2)	Product (3)	Yield(%)
1	Ph-		 **3a**	65
2	p-$CH_3C_6H_4$-		 **3b**	71
3	p-ClC_6H_4-		 **3c**	75
4	PhCH=CH-		 **3d**	53
5	Ph-		 **3e**	54
6	p-$CH_3C_6H_4$-		 **3f**	58
7	p-$CH_3C_6H_4$-		 **3g**	79
8	p-$CH_3C_6H_4$-		 **3h**	66

Yields were not optimized and were referred to as isolated ones after column chromatography on silica gel. All reactions were carried out with 4 mol% of $RuCl_2(PPh_3)_3$ at 90-100°C for 2h.

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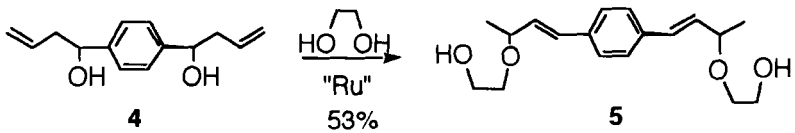
The reaction results are summarized in the Table. Thus, treatment of 1-phenyl-3-buten-1-ol with a catalytic amount of tris(triphenylphosphine)ruthenium (II) dichloride in ethylene glycol at 90-100°C for 2 h generated the monoallylated ether **3a** in 65% isolated yield (entry 1), without any detection of the bis-ether formation. Similar mono-ethers (**3b**, **3c**) were prepared from the reaction of ethylene glycol with 1-(p-methylphenyl)-3-buten-1-ol and 1-(p-chlorophenyl)-3-buten-1-ol (entries 2, 3). Reaction of 1-pheneyl-1,5-hexadien-3-ol with ethylene glycol generated a phenyldienyl alcohol **3d** (entry 4). Ethylene glycol oligomers reacted with homoallyl alcohols similarly, generating the monoalkylated ethers **3e**, **3f**, **3g** and **3h** (entries 5-8).

Other diols were transformed to mono ethers similarly. Compound **4** is transformed to ether **5** under the same reaction conditions. The reaction also showed a high selectivity between primary and secondary hydroxyl groups. Thus, when 1-phenyl-3-buten-1-ol reacted with 1,3-butanediol (**6**), a compound bearing both primary and secondary hydroxyl groups, the reaction occurred exclusively on the primary hydroxyl group to generate mono ether **7**. Upon oxidation with PCC,[5] the mono-ether was transformed to methyl ketone **8** in 75% (Eq. 3). The use of 1-(p-methylphenyl)-3-buten-1-ol gave a 15:1 mixture of products, corresponding to the reaction of primary and secondary hydroxyl groups (Eq. 4). Thus, the study herein provided a new method for the preparation of mono-protected diols.



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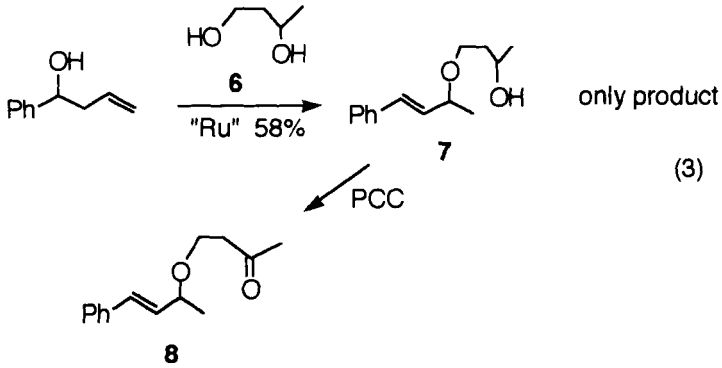

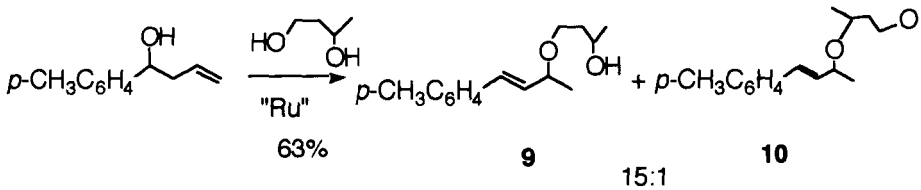

Experimental Section

Commercially available compounds were used without further purification. Flash chromatography employed E. Merck silica gel (Kiesegel 60, 230-400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ from G.E. Omega 400 (400 MHz) instrument, with TMS as an internal standard. Infra-Red spectra were performed on FT-IR (Mattson Cygnus 100). Mass Spectra were measured on a Kratos Mass Spectrometer.

General Procedure for the Alkylation Reaction: A mixture of **1** (1 mmol) and $RuCl_2(PPh_3)_3$[6] (4 mol%) in glycol (3 mL) was stirred at 90-100°C for 2h under an air atmosphere. The reaction mixture was cooled to room temperature, followed by the addition of 1 ml of water and extraction for four times with ether. The combined organic layers were dried over $MgSO_4$ and filtered. Evaporation of

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the solvent gave a crude product which was purified by flash chromatography on silica gel (eluting with hexane and ethyl acetate) to give the mono-ethers.

3a: IR(film): 3441, 1599, 1495, 1450, 1373, 1265, 1105, 1063, 970cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.37(d, J=6,4Hz, 3H), 3.48(m, 1H), 3.65(m, 1H), 3.74(m, 2H), 4.06(m, 1H), 6.09-6.13(dd, J=7.6, 16.0Hz, 1H), 6.53(d, 1H, J:16.0Hz); 7.24-7.40(m, 5H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.62, 62.00, 69.38, 77.11, 126.48, 127.77, 128.60, 131.37, 131.43, 136.48ppm. HRMS: Calc'd for $C_{12}H_{16}O_2$, 192.1151; Found, 192.1150.

3b: IR(film): 3437, 1653, 1616, 1514, 1456, 1265, 1107, 1063, 970cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.36(d, J=6,4Hz, 3H), 2.25(bs, 1H), 2.34(s, 3H), 3.47(m, 1H), 3.64(m, 1H), 3.74(m, 2H), 4.04(m, 1H), 6.04-6.07(dd, J=8.0, 15.8Hz, 1H), 6.51(d, J=15.8Hz, 1H), 7.12-7.28(m, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.20, 21.65, 62.02, 69.32, 77.19, 126.38, 129.29, 130.33, 131.37, 133.68, 137.61ppm. HRMS: Calc'd for $C_{13}H_{18}O_2$, 206.1307; Found, 206.1318. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.68; H, 8.95.

3c: IR(film): 3430, 1651, 1593, 1491, 1460, 1406, 1371, 1265, 1091cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.35(d, J=6.4Hz, 3H), 2.24(bs, 1H), 3.48(m, 1H), 3.60(m, 1H), 3.74(m, 2H), 4.04(m, 1H), 6.06-6.10(dd, J=7.6, 16.0Hz, 1H), 6.47(d, J=16.0Hz, 1H); 7.27-7.30(m, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.50, 61.99, 69.46, 77.05, 122.68, 128.74, 130.07, 132.08, 133.34, 134.99ppm. HRMS: Calc'd for $C_{12}H_{15}O_2Cl$, 226.0761; Found, 226.0759.

3d: IR(film): 3430, 1605, 1450, 1265, 1109, 1059cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.31(d, J=6.4Hz, 3H), 2.05(bs, 1H), 3.45(m, 1H), 3.61(m, 1H), 3.73(m, 2H), 3.98(m, 1H), 5.69-5.72(dd, J=7.6, 15.6Hz, 1H), 6.32-6.36(dd, J=10.4, 15.6Hz, 1H), 6.55(d, J=15.6Hz, 1H), 6.74-6.78(dd, J=10.8, 15.6Hz,

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1H), 7.21-7.40(m, 5H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.50, 62.05, 69.30, 84.44, 126.37, 127.66, 128.08, 128.65, 128.70, 131.82, 132.82, 135.52, 137.06ppm. HRMS: Calc'd for $C_{14}H_{18}O_2$, 218.1307; Found, 218.1302.

3e: IR(film): 3435, 1603, 1450, 1217, 1132, 1064 cm^{-1}. ^1H NMR(400 MHz, $CDCl_3$): δ 1.36(d, J=6.4Hz, 3H), 3.53(m, 2H), 3.62(m, 2H), 3.68(m, 2H), 3.74(m, 2H), 4.05(m, 1H), 6.09-6.13(dd, J=7.6, 16.0Hz, 1H), 6.53(d, J=16.0 Hz, 1H), 7.24-7.40(m, 5H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 21,65, 61.86, 65.11, 70.63, 72.47, 77.28, 126.48, 127.76, 128.44, 128.60, 131.35, 131.50, 136.48ppm. HRMS: Calc'd for $C_{14}H_{20}O_3$, 236.1413; Found, 236.1406.

3f: IR(film): 3450, 1651, 1613, 1514, 1454, 1086 cm^{-1}. ^1H NMR(400 MHz, $CDCl_3$): δ 1.35(d, J=6.4Hz, 1H), 2.33(s, 3H), 2.78(bs, 1H), 3.50-3.73(m, 8H), 4.03(m, J=6.4Hz, 1H), 6.03-6.07(dd, J=7.6, 16.0Hz, 1H), 6.48(d, J=16.0Hz, 1H), 7.12(m, J=8.4Hz, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.21, 21.70, 61.82, 67.60, 70.61, 72.50, 77.36, 126.38, 129.29, 130.30, 131.45, 133.68, 137.59ppm. HRMS: Calc'd for $C_{15}H_{22}O_3$, 250.1569; Found, 250.1566.

3g: IR(film): 3455, 1653, 1613, 1514, 1454, 1350, 1265, 1088 cm^{-1}. ^1H NMR(400 MHz, $CDCl_3$): δ 1.33(d, J=6.4Hz, 3H), 2.32(s, 3H), 2.80(bs, 1H), 3.48-3.72(m, 12H), 4.01(m, 1H), 6.03-6.07(dd, J=8.0, 16.0Hz, 1H), 6.48(d, J=16.0Hz, 1H), 7.2(m, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.21, 21.70, 61.71, 67.44, 70.33, 70.61, 70.71, 72.54, 77.26, 126.37, 129.26, 130.52, 131.25, 133.78, 137.50ppm. HRMS: Calc'd for $C_{17}H_{26}O_4$, 294.1832; Found, 294.1821.

3h: IR(film): 3462, 1651, 1613, 1514, 1452, 1350, 1267, 1120 cm^{-1}. ^1H NMR(400 MHz, $CDCl_3$): δ 1.33(d, J=6.4Hz, 3H), 2.31(s, 3H), 2.92(bs, 1H), 3.48-3.72(m, 16H), 4.01(m, 1H), 6.02-6.06(dd, J=8.0, 16.0Hz, 1H), 6.47(d, J=16.0Hz, 1H), 7.20(m, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.18, 21.67,

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61.66, 67.44, 70.21, 70.50, 70.53, 70.59, 70.69, 72.70, 77.28, 126.37, 129.25, 130.49, 131.28, 133.76, 137.48ppm. HRMS: Calc'd for $C_{19}H_{30}O_5$, 338.2094; Found, 338.2079.

5: IR(film): 3416, 1603, 1439, 1265, 1107, 1062cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.35(d, 6H, J=6.0Hz), 2.212(bs, 2H), 3.47(m, 2H), 3.63(m, 2H), 3.72(m, 4H), 4.05(q, J=6.0Hz, 2H), 6.08-6.12(dd, J=7.2, 15.6Hz, 2H), 6.49(d, J=15.6Hz, 2H), 7.33(s, 4H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.71, 62.37, 69.80, 77.56, 127.46, (129.26, 129.37), 131.73, 132.18, (132.84, 132.93), 136.76ppm. HRMS: Calc'd for $C_{18}H_{26}O_4$, 306.1832; Found, 306.1828.

7: IR(film): 3437, 1653, 1599, 1578, 1495, 1449, 1373, 1319, 1265, 1084cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.20(d, J=6.0Hz, 3H), 1.33-1.35(dd, J=2.4, 6.4Hz, 3H), 1.64-1.80(m, 2H), 1.85(bs, 1H), 3.25-3.56(m, 1H), 3.65-3.79(m, 1H), 4.00(m, 1H), 6.06-6.12(m, 1H); 6.52(d, , J=16.0Hz, 1H), 7.24-7.40(m, 5H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.73, (23.32, 23.35), (38.06, 38.12), (67.28, 68.07), 77.26, 126.48, 127.77, 128.61, (131.17, 131.28), (131.48, 131.54), 136.45ppm. HRMS: Calc'd for $C_{14}H_{20}O_2$, 220.1464; Found, 220.1465.

8: ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.30(d, J=6.4Hz, 3H), 2.18(s, 3H), 2.68(m, 2H), 3.63(m, 1H), 3.74(m, 1H), 4.00(p, J=6.4Hz, 1H), 6.06-6.10(dd, J=7.8, 16.0Hz, 1H), 6.50(d, J=16.0Hz, 1H), 7.29-7.37(m, 5H)ppm. ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.60, 30.52, 43.95, 63.30, 77.00, 126.48, 127.69, 128.58, 131.25, 131.48, 136.56, 207.52ppm. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.65; H, 8.30.

9 (major product): IR(film): 3439, 1653, 1613, 1514, 1454, 1371, 1319, 1085cm^{-1}. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.19(d, J=6.4Hz, 3H), 1.32-1.34(dd, J=2.0, 6.4Hz, 3H), 1.62-1.78(m, 2H), 2.34(s, 3H), 3.24-3.58(m, 1H), 3.66-3.77(m,

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1H), 4.00(m, 1H), 6.01(m, 1H), 6.48(d, J=16.0Hz, 1H), 7.20(m, 4H). ^{13}C NMR(100 MHz, $CDCl_3$): δ (21.23, 21.80), (22.54, 23.33), (38.02, 38.09), (67.24, 67.52), (68.02, 68.13), 77.29, (126.35, 126.40), 129.31, (130.09, 130.20), (131.51, 131.67), 133.63, 137.64ppm. HRMS: Calc'd for $C_{15}H_{22}O_2$, 234.1620; Found, 234.1609. **10** (minor product): IR(film): 3400, 1614, 1510, 1450, 1085cm^{-1}. ^1H NMR(400 MHz, $CDCl_3$): δ 1.18(d, J=5.9Hz, 3H), 1.3(d, J=6.4Hz, 3H), 1.6-1.8(m, 2H), 2.33(s, 3H), 2.6(br, 1H), 3.7-3.9(m, 3H), 4.15(m, 1H), 6.06(dd, J=6.9, 16.0Hz, 1H), 6.48(d, J=16.0Hz, 1H), 7.20(m, 4H). ^{13}C NMR(100 MHz, $CDCl_3$): δ 20.91, 21.20, 21.73, 38.22, 60.87, 72.95, 75.14, 126.33, 129.28, 130.05, 131.35, 133.89, 137.47ppm.

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