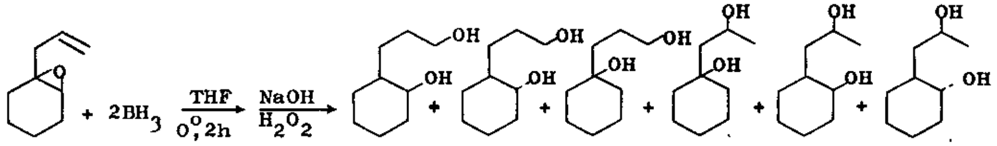
TRANSFORMATION OF ALLYLIC EPOXIDES TO TETRAHYDROFURFURYL ALCOHOLS VIA HYDROBORATION

Marek Zaidlewicz* and Ryszard Sarnowski

Institute of Chemistry, Nicolas Copernicus University, 87-100 Torun, Poland

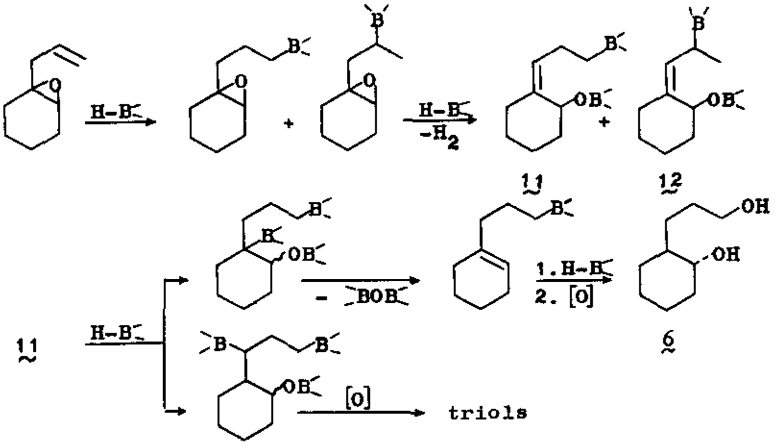
Abstract — The allylic epoxides /1/-/4/ were transformed to the tetrahydrofurfuryl alcohols /17/-/20/, respectively. The formation of /6/ and /10/ in the hydroboration-oxidation of /4/ is interpreted. The monohydroboration-oxidation of /13/ and /14/ gave /15/ and /16/, respectively.

Recently, we reported a convenient stereoselective synthesis of allylic alcohols by the reduction of vinylic epoxides with diborane.[1,2] Extending our study to other unsaturated epoxides, the hydroboration of representative allylic epoxides /1/-/4/ was examined. Stoichiometric experiments /BH_3 in THF, 0°C/ revealed fast /5-10 min/ utilization of one hydride equivalent per mole of the epoxide. In the case of /1/-/3/, the second hydride equivalent was used in 24 h and the reaction stopped at this stage, whereas /4/ used 2.5 hydride equivalents and hydrogen evolution was observed / 0.4 mole of H_2 per mole of the epoxide/. The hydroboration-oxidation products obtained from /4/ were isolated and identified as a mixture /75 % yield/ of /5/-/10/ by glc comparison with authentic samples. In addition to the diols, a mixture of triols was also obtained.



4	5	6	7	8	9	10
	54%	12%	25%	1%	6%	2%

The stereochemistry of /6/ and /10/ ruling out a simple reductive epoxide ring opening and the hydrogen evolution during the reaction may be explained assuming the sequence of transformations involving the intermediates /11/ and /12/. Allylic alcohols of similar structures to /11/ and /12/ have been postulated as the intermediates in the reduction of epoxides with diborane.[3]



The monohydroboration of /1/-/4/ with BH_3/THF followed by standard alkaline hydrogen peroxide oxidation /2 h, 20°C/ gave the corresponding epoxy alcohols and products of their cyclization, e.g. a mixture of 4,5-epoxy-1-pentanol /24 %/, tetrahydrofurfuryl alcohol /70 %/ and 3-hydroxytetrahydropyrane /6 %/ was obtained from /1/. Similarly, /4/ gave 1-/3-hydroxypropyl/-7-oxabicyclo[4.1.0]heptane /27 %/ and 1-oxaspiro[4.5]decan-6-ol /73 %/. By stirring of these mixtures with 3M NaOH solution, the epoxy alcohols were transformed into the cyclic products. Alternatively, the oxidation of the organoboranes derived from /1/-/4/ with hydrogen peroxide in the presence of 100 % excess of sodium hydroxide resulted in the formation of /17/-/20/ as the main reaction products /Table 1/. Small amounts of diols which were *also formed could be separated by distillation*. No attempt was made to optimize the reaction conditions. However, a 10-15 % increase in the yields of the cyclized products was observed when bis-/3-methyl-2-butyl/-borane was used as the hydroborating agent. In a marked contrast, the monohydroboration-oxidation of 5,6-epoxy-1-hexene /13/ and trans-1-methyl-4-isopropenyl-7-oxabicyclo[4.1.0]heptane /14/ carried out under the same conditions as described above gave 5,6-epoxy-1-hexanol /15/ [^{13}C nmr, /$CDCl_3$/, δ, 62.20 /C_1/, 52.41 /C_5/, 47.08 /C_6/, 32.38 and 32.20 /C_2 and C_4/, 22.32 /C_3/] and trans-1-methyl-4-/1-methyl-2-hydroxyethyl/-7-oxabicyclo[4.1.0]heptane /16/ [^1H nmr, /CCl_4/, δ, 0.75 /3H, d, J 6.5 Hz, CH_3/, 1.20 /3H, s, CH_3/, 1.25 - 2.07 /8H, m, CH_2 and CH/, 2.78 /1H, d, J 5.0 Hz, CH-O epoxide/, 3.28 /2H, d, J 5.0 Hz, CH_2-O/, 3.50 /1H, s, OH/] in 75 and 80 % yield, respectively. Clearly, oxidation of the organoborane intermediates derived from /1/-/4/ proceeds with fast cyclization. Cyclzations of

Table 1. Monohydroboration-Oxidation of Allylic Epoxides[a]

epoxide[b]	% product composition		yield[c], %
4,5-epoxy-1-pentene /**1**/	tetrahydrofurfuryl alcohol[e] /**17**/	92	60
	3-hydroxytetrahydropyrane[e]	8	
3,3-dimethyl-4,5-epoxy-1-pentene /**2**/	3,3-dimethyltetrahydrofurfuryl alcohol[f] /**18**/	81	65
	4,4-dimethyl-3-hydroxytetrahydropyrane[f]	6	
	3,3-dimethyl-1,4-pentanediol[g]	13	
4,5-epoxy-4-methyl-1-pentene[d] /**3**/	2-methyltetrahydrofurfuryl alcohol[h] /**19**/	82	60
	2-methyl-1,5-pentanediol[g]	4	
	2-methyl-1,4-pentanediol[g]	6	
	4-methyl-1,4-pentanediol[g]	8	
1-allyl-7-oxabicyclo [4.1.0]heptane /**4**/	1-oxaspiro [4.5]decan-6-ol[i] /**20**/	86	62
	cis-2-/2-hydroxypropyl/-cyclohexanol[g]	5	
	trans-2-/2-hydroxypropyl/-cyclohexanol[g]	3	
	1-/3-hydroxypropyl/-cyklohexanol[g]	3	
	2-/3-hydroxypropyl/-cyclohexanol[g,j]	3	

[a]Hydroborations carried out in THF at 0°C for 2 h, epoxide/BH$_3$ ratio 3 : 1. Oxidation with H$_2$O$_2$ in the presence of 100 % excess of NaOH for 10 h at room temp. [b]Prepared by epoxidation of the corresponding diene with peracetic acid. [c]Isolated yields. [d]Prepared by dehydrochlorination of 1-chloro-4-penten-2-ol[4] with powdered KOH in Et$_2$O. [e]Identified by comparison /glc, ^{13}C nmr/ with the authentic samples. [f]Composition based on ^{1}H nmr and glc. [g]Identified by glc comparison of the diol, its trimethylsilyl ether and trifluoroacetate with the authentic sample. [h]Isolated by distillation, bp 72-73°C /14 mm/, ^{1}H nmr, /CCl$_4$/, δ ,1.12 /3H, s, CH$_3$/, 1.37 - 2,12 /4H, m, CH$_2$-CH$_2$/, 3.32 /2H, s, CH$_2$O/, 3.77 /2H, t, J 6 Hz, CH$_2$O in the ring/, 4.54 /1H, s, OH/. [i]Isolated by distillation, bp 70-72°C /1 mm/, ^{13}C nmr, /CDCl$_3$/, δ , 86.80 /C$_5$/, 74.66 /C$_6$/, 67.61 /C$_2$/, 35.87 /C$_7$/, 31.63 /C$_{10}$/, 28.03, 26.74, 23.84 and 23.78 /C$_3$, C$_4$, C$_8$ and C$_9$/. [j]A mixture of cis and trans isomers.

γ-epoxy alcohols in a basic medium have often been observed previously.[5,6] Although the yields of tetrahydrofurfuryl alcohols obtained in this study are only moderate, the transformation is simple, it can be easily scaled up to molar quantities and it can provide compounds with geminal substituents in the ring.

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