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SYNTHESIS OF ALLYLIC ALCOHOLS via ISOPRENE-, MYRCENE-, OCIMENE-, AND PIPERYLENE-MAGNESIUM COMPLEXES

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Summary. Use of Rieke's active magnesium permits to achieve two-step conversion of the title dienes into respective allylic alcohols 1-11.

Butadiene, isoprene, myrcene, and some other 1,3-dienes react with metallic magnesium; the respective addition compounds have been recently prepared and their interactions with various electrophiles investigated[2,3]. The available data indicate that terminally substituted dienes (e.g.piperylene[3]) react only reluctantly if at all. Therefore it was interesting to examine the Rieke's active magnesium (Mg^*)[4] which was already successfully used for the metalation of butadiene[5]. Our results on the reaction of Mg^* with the title dienes in the presence of $B(OBu^n)_3$ are reported below.

We found that a slightly exothermic reaction takes place upon stirring a suspension of equiv.amounts of freshly prepared Mg^*, diene and $B(OBu^n)_3$ in THF. The reaction mixture was refluxed for ca.1.5h to give, after oxidation with alkaline H_2O_2 solution and column chromatography on alumina, mixture of alcohols[6] (Scheme). Its components were isolated and purified by preparative GLC and/or column chromatography followed by distillation. Their structures were determined spectroscopically (NMR, MS, IR).

Under the above conditions, isoprene gave a mixture of at least six monoterpenols 1-6. The pairs of difficultly separable α- and β-geraniols 3,4 and -nerols 5,6 were identified by direct comparison with authentic samples of α-alcohols[7] and their β-isomers. The known "tail-to-tail" monoterpenol 1 and its α, E-isomer 2 were detected owing to coincidence of their PMR spectra with those reported[8] for these compounds. Their configuration was confirmed by the CMR spectra (Scheme): the diagnostic signals of the allylic atoms $\underline{C}H_3$-C_2 and $\underline{C}H_2O$ for the both substances differ in their chemical shifts by $\Delta\delta \simeq 7.5$ ppm, which is a value characteristic of Z,E isomers[9-11].

Similarly, myrcene was converted into a mixture of geraniol 4 and the previously unknown diterpenols 7[12], b.p.120°/0.7 mm Hg; n_D^{20} 1.4979; M^+290; $\delta_{TMS}^{CCl_4}$: 1.59 (bs, 9H, $C\underline{H}_3$), 1.67 (bs, 6H, $C\underline{H}_3$), 2.05 (m, 12H, $C\underline{H}_2$), 4.00 (bs, 2H, $C\underline{H}_2O$), 5.02 (m, 3H, $\underline{H}C{=}C$), 5.21 ppm (bt, J=7 Hz, 1H, $\underline{H}C{=}C$), and 8[12], b.p.

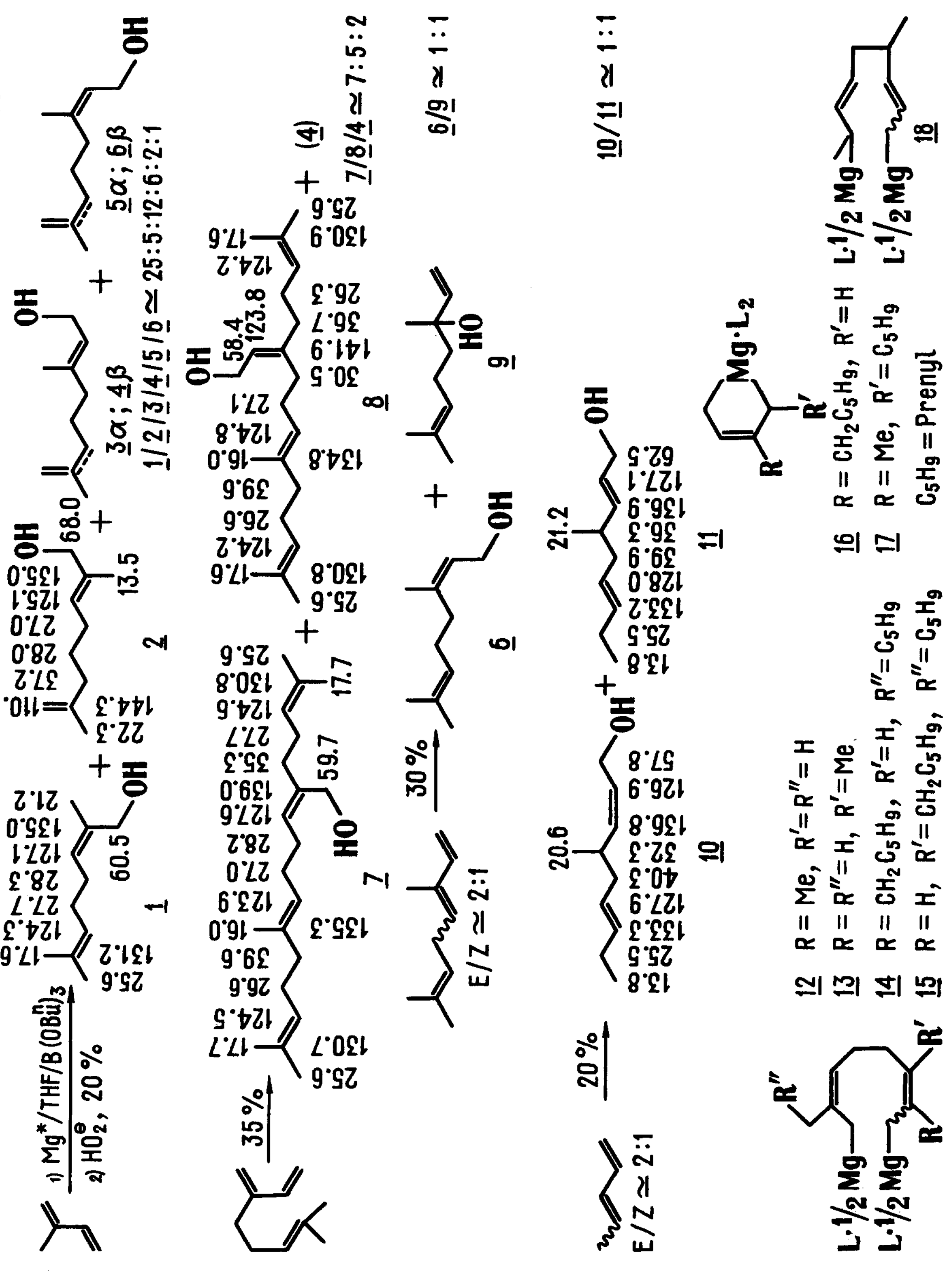
124°/0.75 mm Hg; n_D^{20} 1.4954; M^+290; $\delta_{TMS}^{CCl_4}$: 1.58 (bs, 9H, CH_3), 1.66 (bs, 6H, CH_3), 2.02 (m, 12H, CH_2), 3.99 (bd, J=7 Hz, 2H, CH_2O), 5.03 (m, 3H, HC=C), 5.32 ppm (bt, J=7 Hz, 1H, HC=C)[13]. The additional structural assignments which are based on the CMR data (Scheme) were made both by taking into account the reported chemical shift changes of the allylic carbons for linear terpenols and by comparing the measured δ values with those found in CMR spectra of related substances[10,14]. On this basis, trans,trans configuration of the two central C=C bonds was suggested for the hydroxy bigeranyl 7. Configuration of the prenyl farnesol 8 was formulated by the same way, the hydroxy ethylidene group being assigned to be syn to C_7 since in the CMR spectrum its signal is shifted upfield ($\Delta\delta > 6$ ppm) as compared with the C_5 one.

As anticipated, terminally alkylated dienes react easily with Mg*. Thus, ocimene yielded a mixture of nerol 6 and linalool 9. Similarly, piperylene gave a mixture (ca.1:1) of the previously unknown and difficultly separable alcohols 10,11, b.p. 78°/1 mm Hg, n_D^{20} 1.4665. By precise chromatography of the mixture on alumina, both components of ca.90% purity were isolated: for 10[12] M^+154; $\delta_{TMS}^{CCl_4}$: 0.95 (m, 6H, CH_3), 1.94 (m, 4H, CH_2), 2.40 (m, 1H, CH), 4.03 (bd, J=7 Hz, 2H, CH_2O), 4.97 - 5.61 ppm (m, 4H, HC=CH), and for 11[12] M^+ 154; $\delta_{TMS}^{CCl_4}$: 1.00 (m, 6H, CH_3), 1.99 (m, 4H, CH_2), 2.45 (m, 1H, CH), 4.09(bd, J=7 Hz, 2H, CH_2O), 4.99 - 5.76 ppm (m, 4H, HC=CH). The structure of 10 and 11 was confirmed by their CMR spectra (Scheme) on the basis of the known data on chemical shift changes of allylic carbons in Z,E isomers of 1,2-disubstituted olefins, as well as by comparing the observed δ values with those found in CMR spectra of the parent olefins and alkanes[9,15]. It is noteworthy that the diagnostic signals of C_1 and C_4 atoms for E-11 exhibit downfield shift of $\Delta\delta \geq 4$ ppm as compared with those for Z-10.

Intermediate diene-magnesium complexes[2,3,16] are probably responsible for the formation of the observed products. Thus, an Mg*-initiated "tail-to-tail" and "head-to-tail" dimerization of isoprene and myrcene may lead to the respective addition compounds 12-15. Further oxidative cleavage of the C-B bond, formed by interaction of $B(OBu^n)_3$ with one of the Mg-η^1-allyl bonds and protonolysis of the other, will give rise to alcohols 1-8. It is to be noted that the use of Mg* results mainly in myrcene dimerization, geraniol 4 being generated obviously from the monomeric complex 16. The parent ocimene-magnesium complex 17 could be an intermediate in the formation of terpenols 6,9 whereas isolation of alcohols 10,11 allows to formulate piperylene-magnesium complexes as the "head-to-tail" dimers 18.

Thus, employment of Rieke's active magnesium in the above two-step reaction, carried out virtually as a one batch process, permits to transform

Scheme


1) Mg*/THF/B(OBu^n)3
2) HO2⊖, 20 %
+
OH
17.6
124.3
27.7
28.3
127.1
135.0
21.2
60.5
131.2
25.6
1
110.2
37.2
28.0
27.0
125.1
135.0
68.0
13.5
144.3
22.3
2
3α; 4β
5α; 6β
1/2/3/4/5/6 ≃ 25:5:12:6:2:1
35 %
25.6
130.7
17.7
124.5
26.6
39.6
16.0
135.3
123.9
27.0
28.2
127.6
139.0
59.7
35.3
27.7
124.6
130.8
17.7
25.6
HO
7
17.6
130.8
25.6
124.2
26.6
39.6
16.0
134.8
124.8
27.1
30.5
141.9
58.4
123.8
36.7
26.3
124.2
17.6
130.9
25.6
8
(4)
7/8/4 ≃ 7:5:2
E/Z ≃ 2:1
30 %
6
9
6/9 ≃ 1:1
E/Z ≃ 2:1
20 %
13.8
25.5
133.3
127.9
40.3
32.3
20.6
136.8
126.9
57.8
10
13.8
25.5
133.2
128.0
39.9
36.3
21.2
136.9
127.1
62.5
11
10/11 ≃ 1:1
L·1/2 Mg
L·1/2 Mg
R″
R
R′
12 R = Me, R′ = R″ = H
13 R = R″ = H, R′ = Me
14 R = CH2C5H9, R′ = H, R″ = C5H9
15 R = H, R′ = CH2C5H9, R″ = C5H9
Mg·L2
16 R = CH2C5H9, R′ = H
17 R = Me, R′ = C5H9
C5H9 = Prenyl
18

various 1,3-dienes (including terminally alkylated ones) into allylic alcohols with satisfactory yields.

References and Notes

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