ORGANIC CHEMISTRY

REACTION OF HIGHLY ACTIVE MAGNESIUM WITH ISOPRENE, MYRCENE, OCIMENE, AND PIPERYLENE*

B. A. Cheskis, A. M. Moiseenkov,
M. I. Struchkova, and A. V. Semenovskii[†]

UDC 542.91:546.46:547.315.2

The introduction of highly active magnesium (HM) into chemical practice [2] is apparently a new step in the chemistry of organomagnesium compounds. In the present paper are discussed the results of studying the reaction of HM with isoprene, myrcene, ocimene, and piperylene. It should be mentioned that the metalation of butadiene using HM was accomplished previously [3]. At the same time, data exist [4-8] on the reaction of "classically" activated Mg with a number of 1,3-dienes in the presence of Lewis acids or without them. Here it was found that terminally alklylated dienes do not react [8]. The use of HM removes this limitation.

Slight exoethermic reaction occurs when a suspension of approximatley equivalent amounts of freshly prepared HM, diene, and $B(OBu)_3$ in THF is stirred vigorously. Subsequent reflux of the reaction mass for 1-2 h and decomposition at 0-5°C with alkaline N₂O₂ solution gives a complex mixture of compounds, from which an alcohol fraction was isolated in 20-40% yield by adsorption chromatography on Al₂O₃. Hydrocarbons and glycols were the other reaction products in all cases, which were not studied in detail. The alcohol fraction, which is also usually a complex mixture of compounds, was separated by chromatography, and was analyzed employing mass spectrometry, NMR spectroscopy, and GLC.

With the exception of ocimene, the studied dienes are converted under the reaction conditions predominantly to dimeric alcohols. Thus, isoprene gives a mixture composed of at least six monoterpenols (I)-(VI) in a ratio of (I):(II):(III):(IV):(V):(VI) \simeq 16:3:8:4:2:1. Here it was found that for isoprene, like for all of the other discussed dienes, the observed composition of the alcohols is practically independent of the ratio of the starting reactants under the employed reaction conditions. The structure and composition of the difficultly separable pairs of α - and β -geraniols (III), (IV) and α - and β -nerols (V), (VI) were established by comparing via GLC, IR, and PMR with authentic specimens of the α -alcohols [9] and their β isomers. The ¹³C NMR spectrum, which confirms structures (III) and (V), contains the signals of the C⁷ and C⁸ atoms with δ 144.6 and 110.4 ppm, respectively, and the CH₃-C⁷ signal with δ 22.3 ppm. The chemical shift (CS) values of the five C atoms of the first isoprenoid unit in alcohols (III) and (V) correspond to those reported for the corresponding β -monoterpenols [10-14].



The structure of (I), the main transformation product of isoprene and having a structure of the "tail to tail" type, was established by comparing its PMR spectrum with those published for (I) [15-17] and the corresponding E-isomer [16, 18]. In a similar manner, the structure *See [1] for preliminary communication. [†]Deceased.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 365-371, February, 1981. Original article submitted March 17, 1980. of the α ,E-isomer (II) reliably follows from a comparison of its PMR spectrum with those reported for (II) [19] and its methyl ether [20]. In harmony with [21], the CH_3-C^2 and CH_2O signals in the spectrum of the Z-alcohol (I) are shifted downfield by an average of 0.1 ppm when compared with the corresponding signals of the protons of the E-terpenol (II), whereas the HC³ signals are characterized by a reverse shift of approximately the same magnitude.

The stereochemistry of alcohols (I) and (II) was confirmed by comparing the CS values of the allylic C atoms of CH_3-C^2 and CH_2O , whose signals in the ¹³C NMR spectra of the linear unsaturated terpenols with a cisoid arrangement of the indicated substituents and backbone chain are shifted upfield by 5-8 ppm relative to the corresponding signals in the spectra of the geometric isomers due to the γ -effect [11, 12]. In harmony with these data, and those existing for related structures [12, 13, 23, 24], in the ¹³C NMR spectra of (I) and (II) the signals of the indicated C atoms are located at δ 21.2 and 60.5 ppm, and 13.5 and 68.0 ppm, respectively.

The formation of alcohols (I)-(VI) can be explained by the creation of structures of the "tail to tail" (VII) and "head to tail" (VIII) type, which have the polymeric character of the Z,E-isomers of the dimeric isoprenemagnesium complexes [4, 6, 25], whose hydrolysis previously [4, 5] gave the dimethyloctadienes corresponding to these alcohols. Together with THF, which is used as the solvent, the B(OBu)₃* can also take part in the formation of (VII) and (VIII). Under the influence of the latter the (VII) and (VIII) complexes are apparently converted to the intermediate compounds (IC) (IX) and (X), the protolysis of whose $Mg-n^1-al$ lylic bond [27] and oxidative cleavage of the C-B bond then lead to the observed mixture of primary α - and β -monoterpenols (I)-(VI). The absence in the reaction products of alcohols that could be formed by the boron-allylic rearrangement [28] is evidently explained by the mutual statilization of the Mg- and B-containing fragments in the molecules of the IC (IX) and (X).

A similar study was made of the reaction of HM with myrcene, which leads to a mixture of three primary allylic alcohols in a ratio of $(XI):(XII):(IV) \approx 7:5:2$. The presence of geraniol (IV) was shown by direct comparison with an authentic specimen, while the structure of the previously unknown diterpenols (XI) and (XII) was established mainly via the NMR spectra. Thus, the high resolution PMR spectra indicate that two Me₂C=CH groups and one central isoprenoid E-unit are present in their molecules, since, according to [21], the spectra have broad signals, which differ by ~ 0.05 ppm, from the protons of five CH groups, with a ratio of the integral intensities of the up- and downfield signals equal to 3:2. In the spectra of both alcohols the signal of the CH₂O protons, located at ~ 4.0 ppm, appears as broad singlets for (XI) and as a doublet for (XII). As a result, these data respectively testify to the linear and branched structures of the alcohols with four trisubstituted C=C bonds.

The structure of the irregular diterpenols (XI) and (XII) was confirmed by analyzing their ¹³C NMR spectra, taking into account the known data on the change in the CS of the allylic C atoms in the spectra of the linear unsaturated terpenols and on the basis of comparing the measured CS values with those existing in the literature for related structures [14, 22, 29, 30]. Here the signals with δ 39.6 and 16.0 ppm were assigned to the closely similar allylic C¹² and CH₃-C¹¹ atoms in hydroxybigeranyl (XI) and C¹¹ and CH₃-C¹⁰ atoms in prenylfarnesol (XII), which is equivalent [29] to assigning the E-configuration to the corresponding trisubstituted C=C bonds in these molecules. In addition, the signals with δ 35.3 and 59.7 ppm, present in the spectrum of (XI) and respectively assigned to the allylic C⁵ and CH₂O atoms, make it possible to assume that the hydroxymethylene group is located cisoid relative to the discussed trisubstituted C=C bond. Finally, on the basis of respectively assigning the signals with δ 36.7 and 30.5 ppm in the spectrum of (XII) to the C⁵ and C⁷ atoms, the hydroethylidene group was assigned the syn-configuration relative to the C⁷ center.

Like in the case of isoprene, the progress of the reaction of myrcene with HM can be explained via the step of the dimeric myrcenemagnesium complex (VII) and (VIII) and the Mgand B-containing IC (XIII) and (XIV), which are then converted to (XI) and (XII). From the published analysis data for the hydrolysis products, which contain, in particular, tetraene (XV) [7, 8], corresponding to hydroxybigeranyl (XI), it follows that when the "classically" activated Mg is used the predominant product is the monomeric complex (XVI) and the dimeric complexes of the (VII) and (VIII) type are formed only in small amount. When HM is used these complexes are formed in the reverse ratio, as is evidenced by the relatively low yield of

*Mention was made recently of the role of borates as ligands and activators of Fe- and Ni-containing systems, which catalyze the oligomerization of 1,3-dienes [26]. geraniol (IV), which can be formed in succession from IC (XVI) and (XVII). It should also be mentioned that under our conditions the reaction mixture contains, based on the GLC and PMR data, only trace amounts of myrcenol (XVIII), which is the main product when the monomeric complex (XVI) is treated with Et_20 ·BF₃ and then with alkaline H_20_2 solution [8].





As was indicated above, terminally substituted dienes, except for the polarizable 1,4diphenyl-E,E-butadiene [7], form complexes with the classically activated Mg with difficulty or else they do not react at all with it [8]. We found that HM reacts with ocimene and piperylene under the above indicated conditions to give the complexes in satisfactory yields (in both cases a mixture of the E/Z isomers in an $\approx 2:1$ ratio). Here from ocimene, which was reacted with Mg for the first time, we obtained a mixture ($\sim 1:1$) of nerol (VI) and linalool (XIX), which were easily identified by direct comparison (GLC, PMR) with authentic samples of these monoterpenols:



Their formation can be explained by starting with the monomeric ocimenemagnesium complex (XX) and IC (XXI), in which connection the protolysis and oxidative cleavage of the latter should lead directly to nerol (VI). Linalool (XIX) is more probably formed by a similar transformation of the product of the boron-allylic rearrangement [28] of the IC (XXI), and not by the allylic isomerization of nerol (VI), since geraniol (IV) was not detected in the reaction mixture, which, as is well known [31], is a necessary component of the products of such an isomerization.

HM reacts with a piperviene to give a difficultly separable mixture of previously unknown dimerization products in a ratio of (XXII):(XXII):(XXIV) \approx 7:7:2. The pure (XXIV) and $\sim 90\%$ enriched samples of (XXII) and (XXIII) were isolated by careful chromatography of this mixture on Al₂O₃. The PMR spectra of the latter testify to the presence in the molecules of a secondary methyl, hydroxymethyl, methylene, and ethyl group attached to two 1,2-disubstituted C=C bonds. Their geometry in diene (XXII) is indicated by the IR sepctrum, which contains bands at \vee 730 (cis-C=C) and 975 cm⁻¹ (trans-C=C) the absence of the first band in the spectrum of (XXIII) testifies to the transoid character of both C=C bonds in this diene.

The ¹³C NMR spectra are also in agreement with structures (XXII) and (XXIII). Here, taking into account the known data on the change in the CS of the allylic C atoms in the spectra of the geometric isomers of 1,2-disubstituted olefins and on the basis of comparing the found values with those known for related olefins and alkanes [10, 11, 32, 33], the signals with δ 57.8 and 32.3 ppm were respectively assigned to the C¹ and C⁴ atoms of the Z-fragment in the (XXII) molecules. A shift of the signals of the same C atoms in the spectrum of (XXIII) by 4.5 ppm downfield indicates the E-geometry of the discussed C=C bond. The correspondingly repeating C⁵-C⁹ E-unit in both molecules is characterized by practically coinciding CS values for all five C atoms.

The structure of the secondary alcohol (XXIV) was established in a similar manner, and it was shown to be a mixture of diastereomers in an 065:35 ratio. This follows from a comparison in the PMR spectrum of the integral intensities of the signals of the CH_3-C^6 protons (δ 0.92 and 1.16 ppm) and the multiplet signals from the CHOH protons (δ 3.94 and 4.06 ppm), and here the upfield signals belong to the predominant component. The PMR spectrum also testifies to the presence in the (XXIV) molecule of the CH_2 group and two $CH_3CH=CH$ fragments, in which connection, based on the IR spectral data, one of the C=C bonds in this diene has a cis (730 cm⁻¹), and the other has a trans configuration (975 cm⁻¹). The structure of (XXIV) was confirmed by the ¹³C NMR spectrum, in which, of the two signals of the terminal methyl C atoms with δ 17.4 and 12.8 ppm, the upfield signal was assigned to the C⁹ atom of the Z-ole-finic unit.

The formation of primary allylic alcohols (XXII) and (XXIII) can be depicted on the basis of the "head to tail" dimeric piperylenemagnesium complex (XXV), which is converted by the electrophilic attack of $B(OBu)_3$ on the primary C-Mg bond in IC (XXVI). Correspondingly, cleavage of the secondary C-Mg bond and subsequent boron-allylic isomerization of IC (XXVII) can ultimately lead to the 1,6-dienic carbinol (XXIV).



As a result, the use of HM in the studied reaction makes it possible to obtain in satisfactory yields from 1,3-dienes, including terminally alkylated dienes, a series of substituted 1,5- and 1,6-dienic allylic alcohols, including mono- and diterpenols.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument in CCl₄ solution. The PMR spectra were measured relative to the TMS in CCl₄ solution on Varian DA-60-IL, Tesla BS-497 (100 MHz), and Bruker WH-360 spectrometers. The chemical shifts are given on the δ scale in ppm. The mass spectra were obtained at an ionizing voltage of 70 eV either on a Varian MAT CH-6 or an LKV-2091 chromatomass spectrometer (25 m × 0.25 mm capillary column packed with SE-30). The GLC was run on an LKhM-8MD instrument (2 m × 3 mm column packed with 5% SE-30 deposited on Chromaton N-AW-HMDS). The TLC was run on plates covered with a bound layer of Silufol SiO₂ in the system: 1:1 ether-hexane.

The chromatographic separation of the products was done on neutral Al_2O_3 (I and II activity, 200-250 mesh) using gradient elution with a hexane-ether mixture.

2,7-Dimethyl-2Z,6-octadien-l-ol (I), 2,7-Dimethyl-2E,7-octadien-l-ol (II), α -Geraniol (III), β -Geraniol (IV), α -Nerol (V), and β -Nerol (VI). At $\sim 25^{\circ}$ C, in an argon atmosphere, to a vigorously stirred suspension of HM [2] [freshly prepared by refluxing a suspension of 16 g (169 mmoles) of MgCl₂, 11.4 g (292 mg-atom) of K, and 15.2 g (91.5 mmoles) of KI in 400 ml of THF for 1.5 h] was added in 15 min a mixture of 15.2 g (22.4 ml; 224 mmoles) of isoprene and 29 g (120 mmoles) of B(OBu)₃. The reaction mass was brought up to the boil in 40 min, refluxed for 1 h, cooled, and then treated at $0-5^{\circ}$ with a solution of 18.5 ml of 30% H_2O_2 (163 mmoles) in 61 ml of 10% NaOH solution (152 mmoles) and neutralized with 10% HCl solution. The obtained precipitate was filtered, washed with ether, which was combined with the filtrate, and the aqueous layer was separated and additionally extracted with ether. The combined organic layer was washed with 1% NaHSO₃ solution, then with water, and dried over MgSO₄. After removing the solvent and volatile products in vacuo, the residue (~ 8 g) was chromatographed on 300 g of Al_2O_3 to give 3.55 g (20%) of alcohols (I)-(VI), which were rechromatographed on 300 g of Al₂O₃ to give 1.9 g (11%) of a mixture of (I) [15-17] and (II) [19] in a \sim 5:1 ratio (GLC), 1.2 g (7%) of a mixture of (III) [9] and (IV) in a 2:1 ratio (PMR), bp 96° (5 mm), and 0.3 g (2%) of a mixture of (V) [9] and (VI) in a 2:1 ratio (PMR), bp 92° (5 mm). Additional chromatography of the (I)-(II) mixture on 200 g of Al₂O₃ gave alcohols, respectively, containing 85 and 70% of the main product.

For alcohol (I): bp 72° (2 mm), $R_f 0.37$. Infrared spectrum (ν , cm⁻¹): 840, 890, 910, 940, 1000, 1190, 1380, 1450, 1640, 3360. PMR spectrum (δ , ppm.): 1.59 S, 1.68 s, and 1.74 s (9H, CH₃), 2.02 m (4H, CH₂), 3.98 s (2H, CH₂O), 5.05 t (J = 7 Hz, 1H, HC⁶), 5.19 t (J = 7 Hz, 1H, HC³). ¹³C NMR spectrum (δ , ppm.) 17.6 (CH₃-C⁷), 21.2 (CH₃-C²), 25.6 (C⁸), 27.7 (C⁵), 28.4 (C⁴), 60.5 (C¹), 124.3 (C⁶), 127.1 (C³), 131.2 (C⁷), 135.0 (C²). Mass spectrum (m/e, %) M⁺ 154 (8), 136 (8), 121 (8), 93 (24), 69 (100), 68 (21), 43 (36), 41 (63).

For alcohol (II): bp 74° (2 mm), $R_f 0.35$. Infrared spectrum (v, cm⁻¹): 840, 890, 1000, 1250, 1380, 1450, 1640, 1690, 3360. PMR spectrum (δ , ppm): 1.65 s and 1.68 s (6H, CH₃), 1.65 m and 2.0 m (6H, CH₂), 3.85 s (2H, CH₂O), 4.51 br. s (2H, H₂C=C), 5.32 t (J = 7 Hz, 1H, CH³). ¹³C NMR spectrum (δ , ppm); 13.5 (<u>CH₃-C²</u>), 22.3 (<u>CH₃-C⁷</u>), 27.0 (C⁴), 28.0 (C⁵), 37.2 (C⁶), 68.0 (C¹), 110.3 (C⁸), 125.1 (C³), 135.0 (C²), 144.3 (C⁷). Mass spectrum (m/e, %): M⁺ 154 (8), 136 (17), 121 (19), 93 (32), 69 (100), 68 (36), 55 (42), 43 (70), 41 (92).

2,11,15-Trimethyl-6-hydroxymethylhexadeca-2,6Z,10E,14-tetraene (XI), 2,10,14-Trimethyl-6Z-hydroxyethylidenepentadeca-2,9E,13-triene (XII), and β -Geraniol (IV). At ~25°, in an argon atmosphere, to a vigorously stirred, freshly prepared, as indicated above, suspension of 96 mg-atom of HM was added in 10 min a mixture of 10 g (73.5 mmoles) of myrcene and 19 g (83 mmoles) of B(OBu)₃. The reaction mass was brought up to the boil in 10 min, refluxed for 2 h, worked up as described in the preceding experiment, and the isolated mixture of compounds (12 g) was chromatographed on 400 g of Al₂O₃. We obtained 1.8 g of the starting myrcene and 3.25 g (35%) of a mixture of alcohols (XI), (XII), and (IV), the rechromatography of which on 300 g of Al₂O₃ gave 1.5 g (17%) of (XI), 1.1 g (13%) of (XII), and 0.4 g (5%) of (IV), which was identical (GLC, PMR) with the authentic specimen.

For alcohol (XI): bp120°(0.7 mm), $n_D^{2^0}$ 1.4979, R_f 0.46. Found: C 82.38; H 11.78%. $C_{20}H_{34}O$. Calculated: C 82.69; H 11.80%. Infrared spectrum (v, cm⁻¹): 840, 900, 1010.1110.1380.1450, 1645, 1670, 3520. PMR spectrum (δ , ppm): 1.59 s (9H, CH₃), 1.67 s (6H, CH₃), 2.05 m (12H, CH₂), 4.0 s (2H, CH₂O), 5.02 m (3H, HC=C), 5.21 t (J = 7 Hz, 1H, HC⁷). ¹³C NMR spectrum (δ , ppm): 16.0 (CH₃-C¹¹), 17.1 (CH₃-C² and CH₃-C¹⁵), 25.6 (C¹ and C¹⁶), 26.6 and 27.0 (C⁹ and C¹³), 27.7 (C⁴), 28.2 (C⁸), 35.3 (C⁵), 39.6 (C¹²), 59.7 (CH₂O), 123.9 (C¹⁰), 124.5 and 124.6 (C³ and C¹⁴), 127.6 (C⁷), 130.6 and 130.8 (C² and C¹⁵), 135.3 (C¹¹), 139.0 (C⁶). Mass spectrum (m/e, %): M 290 (0.5), 272 (5), 229 (4), 203 (6), 161 (6), 147 (6), 135 (11), 121 (11), 109 (12), 107 (13), 95 (11), 93 (19), 81 (21), 79 (12), 69 (100), 67 (13), 55 (14), 43 (11), 41 (44).

For alcohol (XI): bp 124° (0.75 mm), $n_D^{2^2}$ 1.4954, R_f 0.39. Found: C 82.42; H 11.84%. $C_{20}H_{34}O$. Calculated: C 82.69; H 11.80%. Infrared spectrum (v, cm⁻¹): 900, 1000, 1110, 1380, 1460, 1650, 1680, 3450. PMR spectrum (δ , ppm): 1.58 s (9H, CH₃), 1.66 s (6H, CH₃), 2.02 m (12H, CH₂), 3.99 d (J = 7 Hz, 2H, CH₂O), 5.03 m (3H, HC=C), 5.32 t (J = 7 Hz, 1H, C=CHCH₂O). ¹³C NMR spectrum (δ , ppm): 16.0 (CH₃-C^{1°}), 17.6 (CH₃-C² and CH₃-C¹⁴), 25.6 (C¹ and C¹⁵), 26.3 and 26.6 (C⁴ and C¹²), 27.1 (C⁸), 30.5 (C⁷), 36.7 (C⁵), 39.6 (C¹¹), 58.4 (CH₂O), 123.9 (CCH₂O), 124.2 (C³ and C¹³), 124.8 (C⁹), 130.8 and 130.9 (C² and C¹⁴), 134.8 (C^{1°}), 141.9 (C⁶). Mass spectrum (m/e, %): M⁺ 290 (0.2), 288 (0.2), 272 (7), 229 (6), 203 (8), 187 (6), 161 (7), 147 (10), 135 (13), 133 (14), 121 (13), 119 (13), 109 (12), 107 (15), 105 (15), 99 (12), 95 (12), 93 (28), 91 (17), 81 (21), 79 (15), 69 (100), 67 (13), 55 (16), 43 (11), 41 (52).

<u> β -Nerol (VI) and Linalool (XIX)</u>. In a similar manner, from 0.1 g-atom of HM, 11.5 g (84 mmoles) of ocimene, and 23 g (0.1 mole) of B(OBu)₃ we obtained 13 g of product, the chromatography of which on 400 g of Al₂O₃ gave 1.3 g of the starting diene and 4.5 g (40%) of a mixture of β -nerol (VI) and linalool (XIX) in a 55:45 ratio, which were identical (GLC, PMR) with authentic specimens of these alcohols.

<u>4-Methylnona-22,6E-dien-1-ol (XXII), 4-Methylnona-2E,6E-dien-1-ol (XXIII), and 6-Methyl-nona-2E,7Z-dien-4-ol (XXIV).</u> In a similar manner, from 0.2 g-atom of HM, 22.8 g (0.336 mole) of piperylene, and 44 g (0.19 mole) of B(OBu)₃ we obtained 10 g of product, the chromatography of which on 300 g of Al₂O₃ gave 5.6 g (\sim 20%) of a mixture of alcohols (XXII)-(XXIV). Rechromatography of this mixture on 400 g of Al₂O₃ gave 0.7 g (2.5%) of (XXIV) and 4.75 g (19%) of a mixture of (XII) and XXIII) in a 1:1 ratio (GLC), bp 76-78° (1 mm), n_D²⁰ 1.4665. Additional chromatography of this mixture on 500 g of Al₂O₃ gave both alcohols \sim 90% pure.

For alcohol (XXII): $R_f 0.36$. Found: C 77.75; H 11.56%. $C_{10}H_{18}O$. Calculated: C 77.86; H 11.76%. Infrared spectrum (ν , cm⁻¹): 730, 975, 1010, 1035, 1250, 1380, 1460, 1660, 3360. PMR spectrum (δ , ppm): 0.95 m (6H, CH₃), 1.94 m (4H, CH₂), 2.40 m (1H, HC⁴), 4.03 d (J = 7 Hz, 2H, CH₂O), 5.0-5.6 m (4H, HC=CH). ¹³C NMR spectrum (δ , ppm): 13.8 (C⁹), 20.6 (CH₃), 25.5 (C⁸), 32.3 (C⁴), 40.3 (C⁵), 57.8 (C¹), 126.9 (C²), 127.9 (C⁶), 133.4 (C⁷), 136.8 (C³). Mass spectrum (m/e, %): M⁺ 154 (0.9), 136 (14), 123 (7), 121 (9), 107 (14), 93 (30), 85 (20), 84 (32), 69 (98), 68 (66), 68 (43), 57 (30), 55 (34), 43 (41), 41 (100).

For alcohol (XXIII): R_f 0.35. Found: C 77.70; H 11.60%. $C_{10}H_{18}O$. Calculated: C 77.86; H 11.76%. Infrared spectrum (v, cm⁻¹): 975, 1010, 1035, 1380, 1460, 1660, 3400. PMR spectrum (δ , ppm): 1.0 m (6H, CH₃), 1.99 m (4H, CH₂), 2.45 m (1H, HC⁴), 4.09 d (J = 7 Hz, 2H, (CH₂O), 5.0-5.8 m (4H, HC=CH). ¹³C NMR spectrum (δ , ppm): 13.8 (C⁹), 21.2 (CH₃), 25.5 (C⁸),

36.3 (C⁴), 39.9 (C⁵), 62.6 (C¹), 127.1 (C²), 127.9 (C⁶), 133.2 (C⁷), 136.9 (C³). Mass spectrum (m/e, %): M⁺ 154(1), 136 (8), 123 (6), 121 (6), 107 /13), 93 (33), 85 (17), 84 (29), 81 (29), 69 (71), 68 (75), 67 (50), 57 (38), 55 (46), 43 (50), 41 (100).

For alcohol (XXIV): bp 64° (1 mm), $n_D^{2^0}$ 1.4612. Rf 0.39. Found: C 77.81; H 11.53%. C₁oH₁₈O. Calculated: C 77.86; H 11.76%. Infrared spectrum (ν , cm⁻¹): 730, 975, 1010, 1060, 1250, 1380, 1460, 1640, 1660, 1670, 3380. PMR spectrum (δ , ppm): 0.92 d and 1.16 d (J = 7 Hz, 3H, CH₃-C⁶), 1.63 m (6H, CH₃C=C), 1.98 m (2H, CH₂), 2.54 m (1H, HC⁶), 3.94 m and 4.06 m (1H, HC⁴), 4.9-5.6 m (4H, HC=CH), ¹³C NMR (δ , ppm): 12.8 (C⁹), 17.4 (C¹), 20.9 (CH₃), 27.8 (C⁶), 44.8 (C⁵), 70.7 (C⁴), 121.9 (C⁸), 125.4 (C²), 135.0 (C⁷), 136.0 (C³). Mass spectrum (m/e, %): M⁺ 154 (0.6), 136 (10), 121 (14), 107 (19), 71 (42), 69 (100), 68 (24), 67 (15), 55 (18), 43 (22), 41 (72).

CONCLUSIONS

1. The metalation of isoprene, myrcene, ocimene, and piperylene using highly active magnesium was studied for the first time.

2. The obtained dienemagnesium complexes were converted in satisfactory yields to the corresponding 1.5- and 1.6-dienic allylic alcohols.

LITERATURE CITED

- 1. A. M. Moiseenkov, B. A. Czeshis, and A. V. Semenovsky, Tetrahedron Lett., 1980, 853.
- 2. R. D. Rieke, Acc. Chem. Res., <u>10</u>, 301 (1977).
- 3. R. G. Salomon, J. Org. Chem., <u>39</u>, 3602 (1974).
- 4. M. Yang, K. Yamamoto, N. Otake, M. Ando, and K. Takase, Tetrahedron Lett., 1970, 3843.
- 5. Y. Nakano, K. Natsukawa, H. Yasuda, and H. Tani, Tetrahedron Lett., 1972, 2833.
- 6. K. Fujita, Y. Ohnuma, H. Yasuda, and H. Tani, J. Organomet. Chem., 113, 201 (1976).
- 7. R. Baker, R. C. Cookson, and A. D. Saunders, J. Chem. Soc. Perkin Trans. 1, <u>1976</u>, 1809, 1815.
- 8. S. Akutagawa and S. Otsuka, J. Am. Chem. Soc., 98, 7420 (1976).
- 9. B. M. Mitzner, V. J. Mancini, and S. Lemberg, Can. J. Chem., 44, 2103 (1966).
- 10. D. E. Dorman, M. Jautelat, and J. D. Roberts, J. Org. Chem., <u>36</u>, 2757 (1971).
- 11. J. W. de Haan and L. J. M. van de Ven, Org. Magn. Reson., 5, 147 (1973).
- 12. E. Wenkert, M. J. Gasic, E. W. Hagaman, and L. D. Kwart, Org. Magn. Reson., 7, 51 (1975).
- 13. F. Bohlmann, R. Zeisberg, and E. Klein, Org. Magn. Reson., 7, 426 (1975).
- 14. L. Crombie, R. W. King, and D. A. Whiting, J. Chem. Soc. Perkin Trans. 1, <u>1975</u>, 914.
- K. Leets, A. Erm, E. Lippmaa, and J. Puskar, Izv. Akad. Nauk Est. SSR, Ser. Khim. Geol., <u>17</u>, 427 (1968).
- 16. S. Watanabe and K. Suga, Austral. J. Chem., 24, 1301 (1971).
- 17. R. Rupprecht and J. Brossas, J. Polym. Sci., Polym. Symp., 52, 67 (1975).
- É. Lippmaa, J. Puskar, K. Leets, and A. Érm, Izv. Akad. Nauk Est. SSR, Ser. Khim. Geol., 18, 321 (1969).
- L. I. Zakharkin, S. A. Babich, and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1976</u>, 1616.
- 20. J. Beger, C. Duschek, and H. Reichel, J. Prakt. Chem., 315, 1077 (1973).
- 21. D. J. Faulkner, Synthesis, 1971, 175.
- 22. C. Nishino and W. S. Bowers, Tetrahedron, 32, 2875 (1976).
- 23. U. Vogeli and W. von Philipsborn, Org. Magn. Reson., 7, 617 (1975).
- 24. W. C. Still and A. Mitra, J. Am. Chem. Soc., 100, 1927 (1978).
- 25. H. Lehmkuhl and D. Reinehr, J. Organomet. Chem., 34, 1 (1972).
- 26. G. A. Tolstikov, U. M. Dzhemilev, S. S. Shavanov, and S. R. Rafikov, Dokl. Akad. Nauk SSSR, 223, 354 (1975).
- 27. S. Akutagawa and S. Otsuka, J. Am. Chem. Soc., 97, 6870 (1975).
- B. M. Mikhailov and Yu. N. Bubnov, Organoboron Compounds in Organic Synthesis [in Russian], Nauka, Moscow (1977), p. 402.
- 29. P. Granger, B. Maudinas, R. Herber, and J. Villoutreix, J. Magn. Reson., 10, 43 (1973).
- 30. T. Kato, H. Takayanagi, T. Uyehara, and Y. Kitahara, Chem. Lett., <u>1977</u>, 1009.
- 31. A. V. Semenovskii, E. V. Polunin, I. M. Zaks, and A. M. Moiseenkov, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1979</u>, 1327.
- 32. J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, J. Am. Chem. Soc., <u>92</u>, 1338 (1970).
- 33. L. P. Lindeman and J. Q. Adams, Anal. Chem., 43, 1245 (1971).