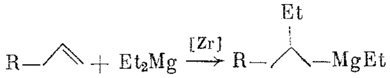
5. L. J. Bellamy, The Infrared Spectra of Complex Molecules, Halsted Press (1975).
6. L. A. Kazitsina and N. B. Kupletskaya, Applications of UV, IR, and NMR Spectroscopy in Organic Chemistry [in Russian], Vysshaya Shkola, Moscow (1971), pp. 28-30.
7. N. A. Eliseev, O. D. Sterligov, G. V. Isagulyants, and I. A. Lozhkina, Calculation of Thermodynamic Parameters for Unsaturated Straight-Chain Hydrocarbons with Nonterminal Double Bonds [in Russian], Izd-vo NTO "Mashprom" (1982), pp. 85-87.

REGIOSELECTIVE REACTION OF FUNCTIONALLY SUBSTITUTED MONO-, DI-, AND TRIOLEFINS WITH ALKYLMAGNESIUM COMPOUNDS, CATALYZED BY Cp_2ZrCl_2

U. M. Dzhemilev, O. S. Vostrikova,
R. M. Sulmanov, A. G. Kukovinets,
and L. M. Khalilov

UDC 542.97:547.313

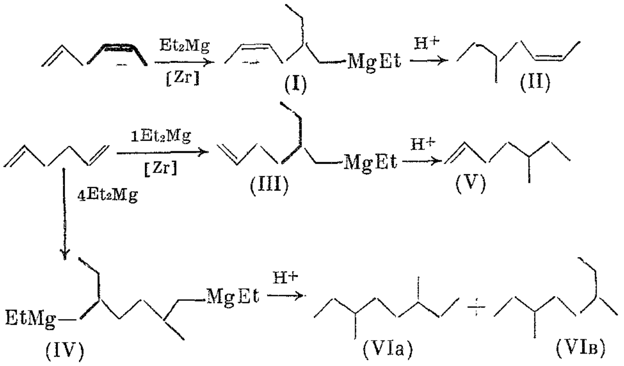
We have recently carried out the selective reaction of α-olefins with Et_2Mg under mild conditions in the presence of catalytic quantities of Cp_2ZrCl_2 [1]



In order to expand the field of application of this method and to investigate the possibility of involving functionally substituted olefins in the reaction with alkylmagnesium compounds, we have studied the reaction of Et_2Mg and EtMgBr with di- and triolefins with different structures, and with O-, N-, S-, and Si-containing unsaturated compounds. The reaction of the selected olefins with Et_2Mg proceeds with maximum selectivity and yield at 20-25° at a Mg:olefin ratio of 1.5:1. However, regardless of the initial reactant ratio, only one of the ethyl groups of the Et_2Mg molecule takes part in the reaction. Evidently, the asymmetrical higher dialkyl Mg derivatives formed in the reaction are less reactive.

Only the terminal double bonds enter into the reaction, while the di- and trisubstituted unconjugated double bonds have practically no effect on the course of the reaction and do not undergo isomerization.

Thus, 1,4-Z-hexadiene reacts with Et_2Mg and is converted to 2-ethyl-4Z-hexen-1-yl-ethyl magnesium (I), the hydrolysis of which leads to 5-methyl-2Z-heptene (II). Under analogous conditions 1,5-hexadiene reacts with Et_2Mg to form, depending on the concentration of the latter, mono-(III) and the adducts (IV):

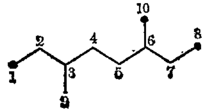
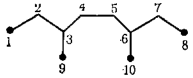
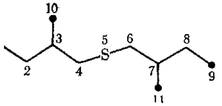
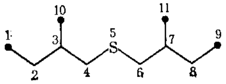
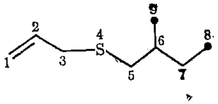
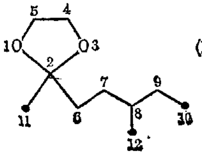


It must be pointed out that the hydrolysis of (IV) gave a mixture of approximately equal amounts of two diastereomers of 3,6-dimethyloctane (VIa, b) which were identified by ^{13}C NMR spectroscopy.

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2053-2060, September, 1984. Original article submitted June 23, 1983.

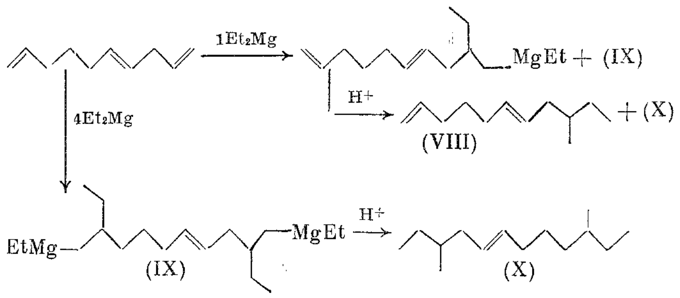
0568-5230/84/3309-1873$08.50

TABLE 1. ^{13}C NMR Spectra of Some Reaction Products with Ethylmagnesium (δ, ppm, CdCl$_3$, signal multiplets)

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}
 (VIa)	11,64qu	29,69t	34,8d	34,03t	34,03t	34,81d	29,69t	11,64qu	19,38qu	19,38 qu	–	
 (VIb)	11,40 qu	29,43t	34,81d	34,03 t	34,03t	34,81d	29,43t	11,40 qu	19,25qu	19,25 qu	–	–
 (XIXa)	11,38qu	28,88t	35,10 d	40,33 t	–	40,33 t	35,10d	28,88 t	11,38qu	18,99 qu	18,99qu	–
 (XIXb)	11,38qu	28,83t	35,10 d	40,28 t	–	40,28 t	35,10 d	28,83 t	11,38qu	18,99qu	18,99qu	
 (XX)	116,55 t	134,76 d	35,35t	–	37,97 t	34,65 t	28,85t	11,36 qu	19,01 qu	–	–	–
 (XXXV)	–	110,33s	–	64,60 t	64,60 t	36,76 t	30,64 t	34,63t	29,43t	11,38qu	27,37qu	19,16qu

The ^{13}C NMR spectra of the mixture of diastereomers (VIa, b) with a ratio of (VIa):(VIb) = 1:1 (Table 1) show a difference between the chemical shifts of the signals of the methyl groups C^1, C^8 by 0.24 ± 0.05 ppm and of the groups C^9, C^{10} by 0.13 ± 0.05 ppm. The chemical shifts of the signals of the methylene carbon atoms C^2 and C^7 differ by 0.26 ± 0.05 ppm. The difference between the signals of the stereoisomer pairs is probably caused by steric interactions of the substituents located at the chiral centers C^3 and C^6. These results can be explained in the light of the fact that the chemical shifts of the ^{13}C nuclei are very sensitive towards steric interactions of groups located at the chiral centers and separated by one or several C atoms [2, 3]. In the case of (VIa, b) the erythro-interaction takes place over three carbon—carbon bonds.

Attempts to achieve a selective reaction of 1,4E,9-decatriene via one of the endstanding double bonds were unsuccessful. Already at a Mg:olefin ratio of ≤ 1, 3,10-dimethyl-5E-dodecene (X) was found in the hydrolysis products together with 9-methyl-1,6E-undecadiene (VIII); this indicates that the reaction with Et_2Mg proceeds simultaneously via both double bonds with the formation of (IX). This compound can be obtained with a quantitative yield when an excess of Et_2Mg (Mg:olefin = 4:1) is used.

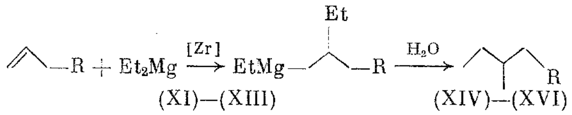


The fact attracts our attention that the reaction of 1,4E,9-decatriene with Et_2Mg proceeds exclusively via the vinyl group located more closely to the trans-disubstituted double bond C^4—C^5.

It must be pointed out that the presence of an acetylene bond or of a conjugated diene system in the molecule of an α-olefin inhibits the reaction with alkyl magnesium compounds. Thus, for instance, 1-decen-4-yne, 4-octyne, 1,3,7-octatriene, and 3-methyl-1,3E,6-heptatriene do not react with stoichiometric amounts of Et_2Mg in the presence of Cp_2ZrCl_2; even when present in catalytic amounts (Zr:diene = 1:1-5) they completely block the reaction of α-olefins at 20-80°.* We did not obtain such an effect when dienes or enynes were substituted by electron donors such as Ph_3P or pyridine.

Furthermore, it was also of interest to carry out the reaction with olefins containing electron donor and electron acceptor functional substituents which were capable of forming complexes with the catalyst atom or the organometallic reagent (Et_2Mg). Allyl chloride, allyl alcohol, diallyl ether, allyl phenyl ether, and diallyl sulfide were chosen as objects of the investigation. It was found that their reactivity depended decisively on the nature of the functional substituent, located in the allyl position to the double bond.

Thus, trimethylallyl silane and N,N-diethylallylamine react quantitatively with Et_2Mg to give the corresponding compounds (XI) and (XII), while the conversion of butyl allyl ether in the reaction with Et_2Mg reaches only 30% in 90 h. Allyl chloride, allyl alcohol, allyl phenyl ether and phenylallyl sulfone do not undergo the reaction at all. Under these conditions allyl acetate is converted to allyl alcohol and diethyl carbinol:

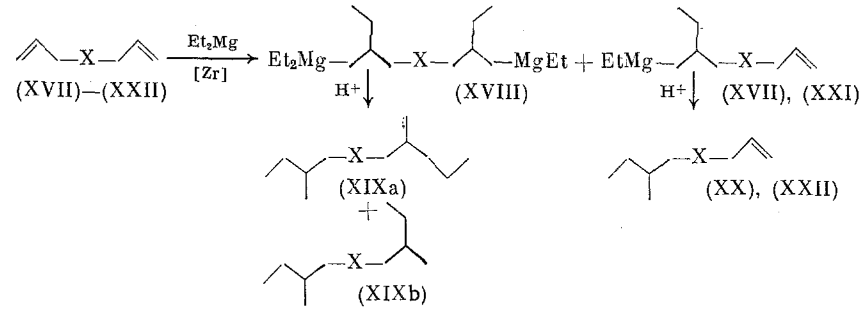


R = NEt_2 (XI), (XIV); $SiMe_2$ (XII), (XV); OBu (XIII), (XVI).

---

*At higher temperatures polymerization of initial olefins and dienes takes place under the influence of Zr complexes.

After 90 h at 25° diallyl sulfide reacts quantitatively with an excess of Et_2Mg to give the mono- and di-derivatives (XVII) and (XVIII) in the ratio 6:4. Under analogous conditions diallyl ether forms with Et_2Mg only the monoaddition product (XXI) with a yield of 40%



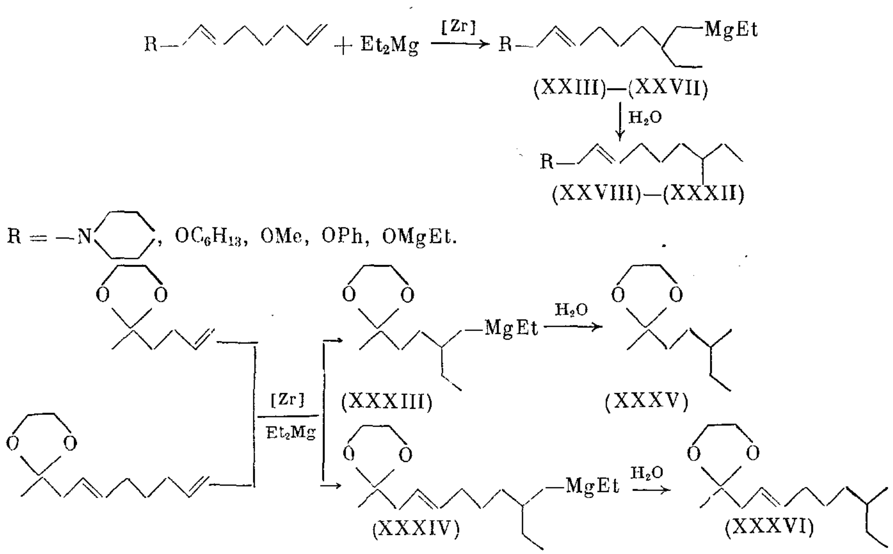
X = S (XVII)—(XX); O (XXI), (XXII).

In analogy to the above-mentioned 3,6-dimethyloctane (VIa, b), dialkyl sulfide (XIXa, b) represents a mixture of equal amounts of two diastereoisomers. In the compounds (XIXa, b) the interaction of the chiral C atoms takes place through four bonds, including two C—S bonds; as a result of this, the ^{13}C NMR spectrum of (XIXa, b) shows only a negligible difference between the chemical shifts of the atoms C^2, C^8, and C^4 which indicates a significant weakening of the erythro-interaction with the increasing number of bonds between the chiral centers (see Table 1).

The results obtained led to the conclusion that electron acceptor substituents at the allyl C atom reduce significantly the activity of the double bond in the reaction with Et_2Mg; on the other hand, the nature of the heteroatom and the structure of the allyl substituent have practically no influence on the regional selectivity of the process.

When investigating the reaction of 2,7-octadiene derivatives we found that the functional substituents which are further removed from the vinyl group have little effect on the reactivity of the latter towards Et_2Mg. Thus, octadienyl ethers of methanol, phenol, and cyclohexanol, as well as 2,7-octadienylpiperidine and 2,7-octadienol react quantitatively via their endstanding vinyl group; this leads to the formation of the corresponding higher asymmetrical compounds with functional substituents (XXIII)-(XXVII). The latter hydrolyze into (XXVIII)-(XXXII).

The presence of an ethylene ketal group in the α-olefin molecule does not inhibit the rapid and selective reaction of 2-ethylenedioxy-5-hexene and 2-ethylenedioxy-4E,9-decadiene with Et_2Mg which gives the corresponding (XXXIII) and (XXXIV) with high yields.



R = —N⟨ ⟩, OC_6H_{13}, OMe, OPh, OMgEt.

It was of interest to compare into more detail the reactivity of Et_2Mg and EtMgBr. Although at 60-65° EtMgBr shows little selectivity as a reagent [1], it was found that at tem-

TABLE 2. Reaction of α-Olefins with EtMgZ in the Presence of Cp_2ZrCl_2 (Mg:Zr = 100:1, R—:Mg = 1:1.5, 20°, ether)

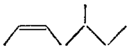
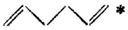
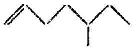
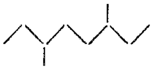
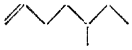
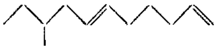
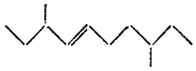
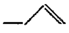
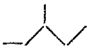
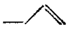
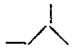
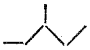
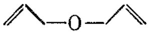
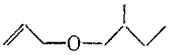
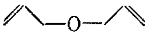
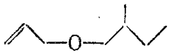
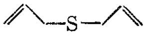
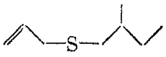
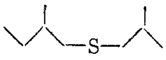
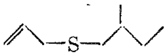
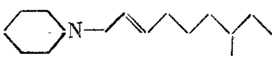
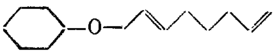
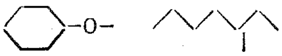
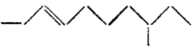
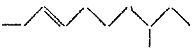
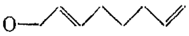
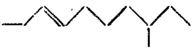
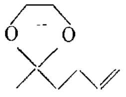
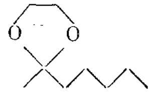
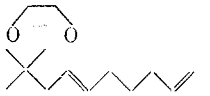
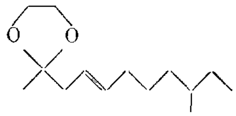
Initial olefin	Z	Duration of experiment, h	Olefin conversion, %	Hydrolysis product	
				structure	yield, %
Octene-1	Et	2	100		98
Same	Br	6	35	Same	30
	Et	2	95		90
	Et	4	45		40
Same†	Et	2	95		90
» *	Br	14	50		40
	Et	2	80		75
Same†	Et	4	98		80
Et$_2$N —	Et	4	100	Et$_2$N 	98
Me$_3$Si —	Et	4	96	Me$_3$Si 	96
Bu—O —	Et	90	30	Bu—O —	30
	Et	60	30		30
	Et	90	40		40
	Et	4	25		22
Same†	Et	90	95	 and 	95
	Et	4	98		98
Same	Br	24	90	Same	90
	Et	4	95		95
Same	Br	24	90	Same	90
MeO —	Et	4	98	MeO—	95
Same	Br	20	90	Same	90
PhO— 	Et	4	95	PhO—	90
HO—	Et	4	98	HO—	98

TABLE 2 (Continued)

	Et	4	95		95
	Br	20	95	Same	95
	Et	6	98		98

*Mg:olefin = 1:1.
†Mg:olefin = 4:1.

peratures not exceeding 25° the regional selectivity of the reactions with Et_2Mg and EtMgBr was the same. A longer time is required to achieve a high conversion of the initial olefins with the latter reagent (Table 2). Only half of the ethyl groups in the EtMgBr molecules participate in the reaction. It can be assumed that in these reactions EtMgBr is first disproportionated into $MgBr_2$ and Et_2Mg under the action of Cp_2ZrCl_2; Et_2Mg then reacts further with the olefin.

EXPERIMENTAL

The experiments were carried out in a dry argon atmosphere. The ether and the initial olefins were distilled immediately before use over $LiAlH_4$ in a stream of Ar. Et_2Mg was prepared by disproportionation of EtMgBr according to [4]. The yields of the Mg derivatives were determined from their hydrolysis products with reference to the original olefin. n-Decane was used as the internal standard, n-octane in the tests with 1-octene. Gas–liquid chromatography (GLC) was performed on a "Khrom-5" chromatograph with a flame ionization detector; the column was 3.7 × 3 mm, packed with 15% PEG-6000 on Chromaton N-AW. The PMR spectra were recorded on a "Tesla BS-487B" spectrometer (60 MHz) with HMDS as the internal standard. The ^{13}C NMR spectra were recorded in $CdCl_3$ on a "Jeol FX-90Q" with broad-band suppression and in the monoresonance regime with partial retention of the Overhauser effect. The mass spectra were obtained on a MKh-1306 spectrometer with an electron ionization energy of 70 eV at 150°.

Carbometallization of α-Olefins. A solution of 15 mmole Et_2Mg or EtMgBr in 15 ml ether is treated consecutively with 0.1 mmole Cp_2ZrCl_2 and 10 mmole olefin. The solution is stirred for the time required at 20-25°, cooled to 0°, and decomposed with a saturated NH_4Cl solution. The organic layer is separated, dried with $MgSO_4$, and analyzed by GLC. The hydrocarbons are separated by vacuum distillation and identified by its spectral characteristics. The yields of the reaction products are given in Table 2, the ^{13}C NMR spectra of compounds (VI), (XIX), (XX), and (XXXV) in Table 1. The purity of the separated hydrocarbons was not less than 98%.

5-Methyl-2Z-heptene (II), bp 44° (47 mm), n_D^{20} 1.4185. IR spectrum (ν, cm^{-1}): 750, 3030 (cis–CH=CH). PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.15 m (3H, CH_2, CH), 1.53 d (3H, CH_3), 1.93 m (2H, CH_2C=), 5.33 m (2H, CH=CH). M^+ 112.

5-Methyl-1-heptene (V), bp 40° (55 mm), n_D^{20} 1.4105. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH=CH_2$). PMR spectrum (δ, ppm): 0.89 m (6H, CH_3), 1.25 m (5H, CH_2, CH), 2.01 m (2H, CH_2C=), 4.9-6.1 m (3H, $CH=CH_2$). M^+ 112.

Mixture of Stereoisomeric 3,6-Dimethyloctanes (VIa, b), bp 64° (55 mm), n_D^{20} 1.4155. PMR spectrum (δ, ppm): 0.89 m (12H, CH_3), 1.22 m (10H, CH_2, CH). M^+ 142.

9-Methyl-1,6E-undecadiene (VIII), bp 86° (13 mm), n_D^{20} 1.4180. IR spectrum (ν, cm^{-1}): 975, 3030 (trans–CH=C), 920, 1000, 3080 ($CH=CH_2$). PMR spectrum (δ, ppm): 0.9 m (6H, CH_2), 1.30 m (5H, CH_2, CH), 2.02 m (6H, CH_2C=), 4.92-6.25 m (5H, CH=CH, $CH=CH_2$). M^+ 166.

3,10-Dimethyl-5,E-dodecene (X), bp 134° (13 mm), n_D^{20} 1.4187. IR spectrum (ν, cm^{-1}): 975, 3030 (trans–CH=CH). PMR spectrum (δ, ppm): 0.91 m (12H, CH_3), 1.26 m (10H, CH_2, CH), 1.98 m (4H, CH_2C=), 5.45 m (2H, CH=CH). M^+ 196.

(2-Methylbutyl)-N,N'-diethylamine (XIV), bp 147.5° (760 mm), n_D^{20} 1.4185. PMR spectrum (δ, ppm): 0.9 m (9H, CH_3), 1.06 m (3H, CH_2, CH), 2.35 m (6H, CH_2) . M^+ 143.

(2-Methylbutyl)trimethylsilane (XV), bp 116° (760 mm), n_D^{20} 1.4262. PMR spectrum (δ, ppm); 0.05 s (9H, CH_3), 0.5 m (2H, CH_2Si), 0.82 m (6H, CH_3). 1.12 m (3H, CH_2). M^+ 144.

(2-Methylbutyl)butyl Ether (XVI), bp 38° (52 mm), n_D^{20} 1.4060. PMR spectrum (δ, ppm): 0.85 m (9H, CH_3), 1.44 m (7H, CH_2), 3.05 m (2H, CH_2O), 2.25 m (2H, CH_2O). M^+ 144.

(2-Methylbutyl)allyl Sulfide (XX), bp 72° (22 mm), n_D^{20} 1.4695. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$). PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.30 m (3H, CH_2, CH), 2.28 qu (2H, SCH_2C), 2.97 d (2H, $SCH_2C{=}$), 4.83-6.08 m (3H, $CH{=}CH_2$). M^+ 144.

Di-(2-Methylbutyl) Sulfide (mixture of enantiomers XIXa, b), bp 100° (22 mm), n_D^{20} 1.4570. PMR spectrum (δ, ppm: 0.84 m (12H, CH_3), 1.28 m (6H, CH_2, CH), 2.30 qu (4H, SCH_2C). M^+ 174.

(2-Methylbutyl)allyl Ether (XXII), bp 50° (54 mm), n_D^{20} 1.4170. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$), 1100 (O). PMR spectrum (δ, ppm): 0.89 m (6H, CH_3), 1.23 m (3H, CH_2, CH), 3.21 d (2H, OCH_2C), 4.1 m (2H, $OCH_2C{=}$), 5.0-6.25 m (3H, $CH{=}CH_2$). M^+ 128.

1-Piperidyl-7-methyl-2E-nonene (XXVIII), bp 113° (2 mm), n_D^{20} 1.4690. IR spectrum (ν, cm^{-1}): 975, 3030 ($CH{=}CH$). PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.25 m (7H, CH_2, CH), 1.47 m (6H, ring CH_2), 1.98 m (2H, $CH_2C{=}$), 2.28 m (4H, CH_2N), 2.78 m (2H, $NCH_2C{=}$), 5.45 (2H, $CH{=}CH$). M^+ 223.

1-Cyclohexyloxy-7-methyl-2E-nonene (XXIX), bp 122.5° (1.5 mm), n_D^{20} 1.4640. IR spectrum (ν, cm^{-1}): 975, 3030 ($CH{=}CH$). PMR spectrum (δ, ppm): 0.83 m (6H, CH_3), 1.23 m (7H, CH_2), 1.80 m (10H, ring CH_2), 3.15 m (1H, CHO), 3.80 m (2H, $OCH_2C{=}$), 5.5 m (2H, CHCH). M^+ 238.

1-Methoxy-7-methyl-2E-nonene (XXX), bp 65° (5 mm), n_D^{20} 1.4365. PMR spectrum (δ, ppm): 0.87 m (6H, CH_3), 1.23 m (7H, CH_2, CH), 2.0 m (2H, $CH_2C{=}$), 3.35 s (3H, CH_3O), 4.08 m (2H, $OCH_2C{=}$), 5.5 m (2H, $CH{=}CH$). M^+ 170.

1-Phenoxy-7-methyl-2E-nonene (XXXI), bp 185° (7 mm), n_D^{20} 1.5505. IR spectrum (ν, cm^{-1}): 975, 3030 (trans-$CH{=}CH$). PMR spectrum (δ, ppm): 0.91 m (6H, CH_3), 1.3 m (7H, CH_2, CH), 2.10 m (2H, $CH_2C{=}$), 4.53 d (2H, $OCH_2C{=}$), 6.93-7.53 m (5H, C_6H_5). M^+ 232.

1-Hydroxy-7-methyl-2E-nonene (XXXII), bp 114° (10 mm), n_D^{20} 1.4545. IR spectrum (ν, cm^{-1}): 975, 3030 (trans-$CH{=}CH$), 1100, 3400 (OH). PMR spectrum (δ, ppm): 0.88 m (6H, CH_3), 1.25 m (7H, CH_2, CH), 2.01 m (2H, $CH_2C{=}$), 3.4 s (1H, OH), 3.96 m (2H, $OCH_2C{=}$), 5.85 m (2H, $CH{=}CH$). M^+ 156.

2-Ethylenedioxy-5-methylheptane (XXXV), bp 79° (9 mm), n_D^{20} 1.4320. PMR spectrum (δ, ppm): 0.86 m (6H, CH_3), 1.18 s (3H, CH_3), 1.37 m (7H, CH_2, CH), 3.81 s (4H, OCH_2CH_2O). M^+ 172.

2-Ethylenedioxy-9-methyl-4E-undecene (XXXVI), bp 70° (3 mm), n_D^{20} 1.460. IR spectrum (ν, cm^{-1}): 975, 3030 (trans-$CH{=}CH$). PMR spectrum (δ, ppm): 0.90 m (6H, CH_3), 1.20 s (3H, CH_3), 1.30 m (7H, CH_2, CH), 2.0 m (2H, $CH_2C{=}$), 2.23 m (2H, $CH_2C{=}$), 3.83 s (4H, OCH_2CH_2O), 5.41 m (2H, $CH{=}CH$). M^+ 226.

CONCLUSIONS

1. In the presence of catalytic quantities of Cp_2ZrCl_2 Et_2Mg and EtMgBr react regioselectively with α-olefins with different structures to form higher asymmetrical organomagnesium compounds.

2. Electron acceptor substituents at the allyl atom reduce noticeably the activity of the double bond in the reaction with the alkyl magnesium compounds; the nature of the allyl substituent has practically no influence on the regioselectivity of the process. Functional substituents removed from the vinyl group have little influence on the reactivity of the latter in the reaction with the alkyl magnesium compounds.

3. The presence of an acetylenic bond in the α-olefin molecule or of a conjugated double bond system inhibit this reaction.

LITERATURE CITED

1. U. M. Dzhemilev, O. S. Vostrikova, and R. M. Sultanov, Izv. Akad. Nauk SSSR, Ser. Khim., 218 (1983).
2. H. J. Schneider and M. Lonsdorfer, Org. Mag. Reson., 16, 133 (1981).
3. F. G. Yusupova, G. V.Nurtdinova, I. N. Brui, A. N. Nizamova, M. L. Khalilov, G. A. Gailyunas, and V. P. Yur'ev, Zh. Obshch. Khim., 1, 1807 (1981).
4. W. Strohmeier and F. Seifert, Chem. Ber., 94, 2356 (1961).