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Catalytic Hydromagnesiation of 2-Alkylbutadienes

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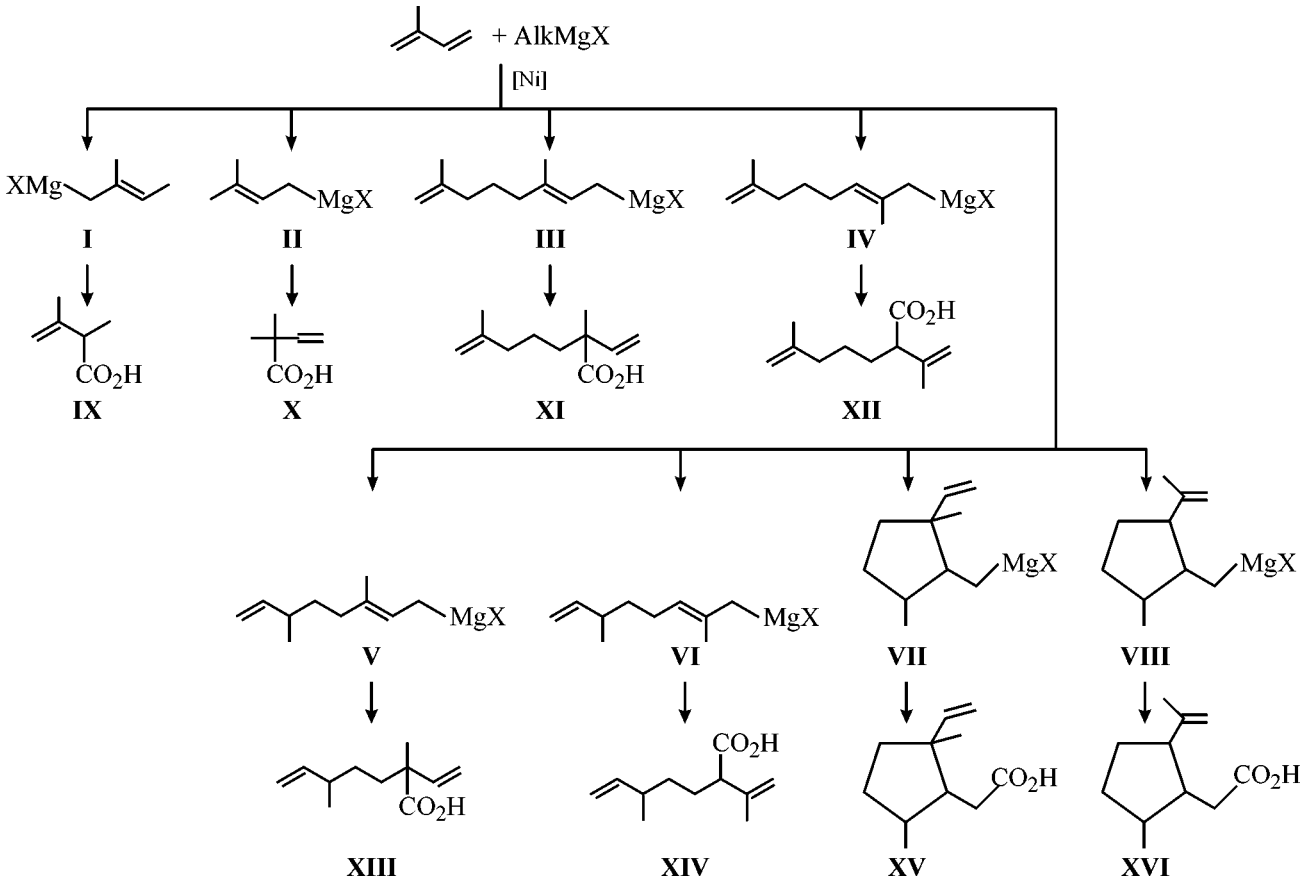
Abstract—The effect of alkyl substituents in 2-alkylbutadienes on their hydromagnesiation with alkylmagnesium halides was studied.

Our studies of the reaction of isoprene with alkylmagnesium halides in the presence of transition metal complexes [1, 2] showed that the major reaction pathway is hydromagnesiation of the diene with formation of linear products containing both dimeric 3,7-dimethyl-2,7-octadienylmagnesium halide and monomeric 2- and 3-methyl-2-butenylmagnesium halides. At the same time, telomeric products were also detected. They formed in smaller amounts, and their relative content largely depended on the reaction conditions and nature of the alkylmagnesium halide and catalyst. To obtain additional data on the reaction mechanism and determine conditions for preparing hydromagnesiation products of the required structure, we considered in detail the influence of the reaction conditions on the composition and structure of 2-alkylbutadiene hydromagnesiation products.

Hydromagnesiation of isoprene (see scheme) can yield two products of the type $H(C_5H_8)_1MgX$ (**I, II**) and six products of the type $H(C_5H_8)_2MgX$ (**III**–**VIII**). By carboxylation of the reaction mixture, organomagnesium compounds **I**–**VIII** are converted to carboxylic acids **IX**–**XVI**.



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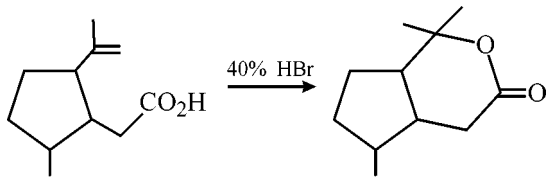
The simplest reaction pattern is observed with the system RMgBr–ether–Ni$(PPh_3)_2Cl_2$. In the fraction of carboxylic acids $H(C_5H_8)_2CO_2H$, the major component (54%) is known 3,7-dimethyl-1,7-octadiene-3-carboxylic acid **XI**. The structure of the second component (27%) was determined as follows. The ^{13}C NMR spectrum of the mixture, after subtraction of the signals of **XI**, contains five medium-intensity signals in the alkyl region (CH_3, $2CH_2$, CH), two signals in the olefinic region (CH_2, C), and a signal of the carboxy group. Since this fraction, according to elemental analysis, consists exclusively of the isomeric acids $H(C_5H_8)_2CO_2H$, we thoroughly looked for the three lacking ^{13}C signals. Remeasurement of particular regions of the ^{13}C NMR spectrum showed that the sought-for three signals overlap with the corresponding signals of the major isomer, **XI**: δ_C 21.9 (CH_3C^7), 144.8 (C^7), and 110.2 ppm (C^8). Along with the overestimated integral intensity of the $CH_2=C^7$ signal of **XI** in the ^{13}C NMR spectrum of the mixture, these facts show that in the isomer under consideration the isoprene unit remote from the carboxy group is identical to that in **XI**. The C–H correlation NMR experiment allowed reliable identification of the second component as 2,7-dimethyl-1,7-octadiene-3-carboxylic acid **XII**, whose precursor is 2,7-dimethyl-2,7-octadienylmagnesium halide **IV**.

In the ^{13}C NMR spectrum of the $H(C_5H_8)_2CO_2H$ acid fraction consisting mainly of acids **XI** and **XII**, there are also weak signals from two more unsaturated carboxylic acids (δ_C 180.8 and 180.9 ppm). As follows from indirect evidences, these carboxylic acids are formed from nonallylic organomagnesium compounds; with *i*-PrMgCl used as the initial alkylmagnesium halide, their content is appreciably larger. To isolate these two acids, we treated the reaction mixture isoprene–*i*-PrMgCl–ether–Ni$(PPh_3)_2Cl_2$ with trimethylchlorosilane to selectively scavenge allylic Grignard reagents **III** and **IV**. Subsequent carboxylation gave a mixture of two carboxylic acids **XV** and **XVI**.

Elemental analysis of this mixture gave the empirical formula $C_{11}H_{18}O_2$, consistent with the composition $H(C_5H_8)_2CO_2H$. The ^{13}C NMR spectrum showed the absence of acids **XI** and **XII** and the presence of two new acids giving the above-mentioned signals at 180.8 and 180.9 ppm. The ratio of **XV** and **XVI** depends on the nature of the initial alkylmagnesium halide, which allowed us to distinguish, basing on the ratio of the integral intensities, two sets of signals corresponding to acids **XV** and **XVI**.

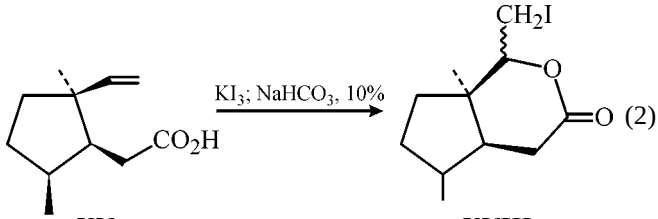
Examination of the olefinic region of the ^{13}C NMR spectrum shows that each acid contains one double bond: $CH=CH_2$ and $C=CH_2$. These fragments give the corresponding signals in the ^1H NMR spectrum. These results, in combination with analytical data, suggest the presence in both acids of a cyclic fragment. Further analysis of the structure of these two cyclic acids by such NMR techniques as dept-135 and C–H and H–H correlations allowed identification of **XV** as 2-(2,5-dimethyl-2-vinylcyclopentyl)acetic acid and of **XVI** as 2-(5-methyl-2-isopropenylcyclopentyl)-acetic acid (Table 1).

In some cases, olefins can be separated by selective addition of electrophilic agents, as different types of C=C bonds react at different rates [3]. Our attempt to selectively add HCl to the disubstituted double bond in **XVI** failed: both acids **XV** and **XVI** remained unchanged. At the same time, after prolonged shaking of a mixture of **XV** and **XVI** with a concentrated HBr solution we obtained a mixture consisting of unchanged **XV** and the cyclization product of **XVI**, (4a,5,7a)-1,1,5-trimethylperhydrocyclopenta[*c*]pyran-3-one **XVII** [reaction (1)]. The mixture of **XV** and **XVII** can be readily separated by selective uptake of **XV** with aqueous alkali.



XVI **XVII** (1)

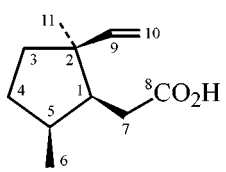
The NMR spectrum of **XV** showed that it is a mixture of two stereoisomers in a ~10 : 1 ratio. The minor isomer gives weak signals of the vinyl group in the ^{13}C NMR spectrum at δ_C 112.0 (CH_2) and 144.4 ppm (CH). The major isomer of **XV** readily undergoes iodolactonization (2), which proves the *cis* arrangement of the reacting groups relative to the ring plane [4].



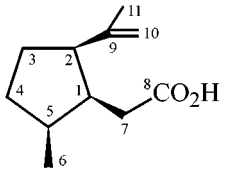
XV **XVIII** (2)

The *cis* arrangement of CH_3C^5 relative to the two above-mentioned substituents follows from the C^1H proton chemical shift in **XV**, 1.61 ppm (Table 1). If the two methyl groups, CH_3C^2 and CH_3C^5, were located on the same side of the ring plane, the C^1H proton would give the signal at about 1.0 ppm [5, 6]. Hence, the major isomer of **XV** is [(1*SR*,2*SR*,5*SR*)-2,5-dimethyl-2-vinylcyclopentyl]acetic acid.

Table 1. ^1H and ^{13}C NMR spectra of **XV** and **XVI**



XV



XVI

^{13}C NMR spectrum, δ_C, ppm	^1H NMR spectrum, δ, ppm (J, Hz)	^{13}C NMR spectrum, δ_C, ppm	^1H NMR spectrum, δ, ppm (J, Hz)
53.6 (CH)	1.61 m	44.7 (CH)	2.09 m
47.8 (C)	–	48.4 (CH)	2.65 m
37.9 (CH_2)	1.53 m and 1.64 m	28.1 (CH_2)	1.59 m and 1.72 m
31.4 (CH_2)	1.26 m and 1.90 m	32.7 (CH_2)	1.17 m and 1.97 m
39.6 (CH)	1.70 m	38.9 (CH)	1.84 m
19.8 (CH_3)	1.00 d (6.5)	21.8 (CH_3)	1.02 d (5.8)
34.9 (CH_2)	2.12 d.d (7.0; 15.6) 2.30 d.d (6.2; 15.6)	35.2 (CH_2)	2.02 d.d (14.4; 5.3), 2.19 d.d (14.4; 4.1)
180.9 (C)	11.8 br.s	180.8 (C)	11.8 br.s
143.3 (CH)	5.80 d.d (11.1; 17.5)	145.6 (C)	–
112.2 (CH_2)	4.95 d (17.5), 4.99 d (11.1)	111.5 (CH_2)	4.67 s and 4.81 s
24.9 (CH_3)	1.11 s	23.0 (CH_3)	1.70 s

Table 2. Yields of products of isoprene hydromagnesiation with different alkylmagnesium halides RMgX (1 mol % $Ni(PPh_3)_2Cl_2$, isoprene : RMgX 1 : 1, 48 h, 18–20°C)

RMgX	**IX + X (IX/X)**	Σ Acids[a]	Content of indicated $H(C_5H_8)_2CO_2H$ isomer, %[b]					
			XI	**XII**	**XIII**	**XIV**	**XV**	**XVI**
In ether								
MeMgBr	–	–						
EtMgCl	Traces	20	54	25	–	–	7	4
EtMgBr	″	26	50	24	5	–	6	10
PrMgCl	5 (3 : 1)	35	51	25	Traces		7	7
PrMgBr	5 (2.5 : 1)	28	54	27	–	–	7	7
PrMgI	–	4	49	30	5	–	3	3
i-PrMgCl	–	35	41	15	Traces		14	20
i-PrMgBr	Traces	22	50	14	3	–	9	24
i-BuMgCl	–	5						
s-BuMgCl	3 (1 : 1)	28	40	10	–	–	19	30
In THF								
MeMgBr	–	–						
EtMgCl	4 (1.5 : 1)	26	57	15	22	Traces	5	Traces
EtMgBr	6 (2 : 1)	22	44	24	19	″	Traces	″
PrMgCl	5 (2 : 1)	33	56	22	8	3	3	3
PrMgBr	4 (2 : 1)	28	55	23	10	7	Traces	Traces
i-PrMgCl	9 (2.5 : 1)	41	40	17	18	7	4	4
i-PrMgBr	Traces	37	42	15	14	14	5	5
i-Pr_2Mg	″	26	46	12	16	20	Traces	5
s-BuMgCl	″	11	29	20	14	17	2	8
s-BuMgBr	–	–						

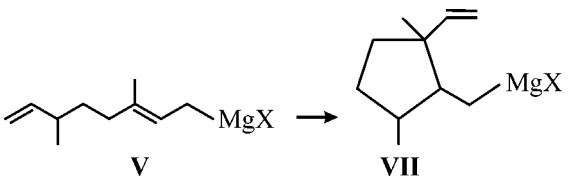
[a] Here and in Tables 3 and 4, $H(C_5H_8)_2CO_2H$ acids are meant. [b] Here and in Tables 3 and 4, the quantitative composition of the mixture of $H(C_5H_8)_2CO_2H$ acids was determined by integration of the ^1H NMR spectra.

Table 3. Yields of products of isoprene hydromagnesiation with different alkylmagnesium halides RMgX (1 mol % $NiPy_4Cl_2$, isoprene : RMgX 1 : 1, 48 h, 18–20°C)

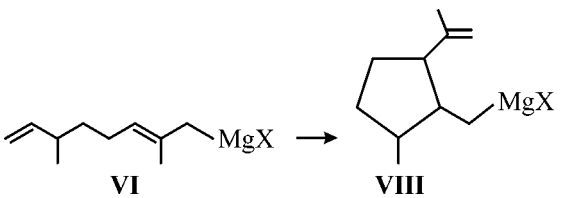
RMgX	In ether		In THF							
	IX + X (IX/X)	Σ Acids	**IX + X**	Σ Acids	content of indicated $H(C_5H_8)_2CO_2H$ isomer, %					
					XI	**XII**	**XIII**	**XIV**	**XV**	**XVI**
MeMgBr	–	–	–	–						
EtMgCl	7 (3 : 1)	Traces	8 (2.5 : 1)	13	30	20	18	5	4	Traces
EtMgBr	17 (1.5 : 1)	″	19 (2 : 1)	7	20	10	35	10	3	3
PrMgCl	5 (2 : 1)	″	12 (2.5 : 1)	17	30	15	17	6	4	4
PrMgBr	10 (2 : 1)	″	8 (4 : 1)	2						
PrMgI	4 (2 : 1)	–								
i-PrMgCl	5 (2 : 1)	Traces	17 (3 : 1)	12	10	5	40	5	Traces	Traces
i-PrMgBr	11 (2 : 1)	″								
i-Pr_2Mg			19 (1.5 : 1)	Traces						
i-BuMgCl	3 (2.5 : 1)	–								
s-BuMgCl	8 (1 : 1)	–	15 (4 : 1)	–	–	–	–	–	–	–
s-BuMgBr			19 (4 : 1)	–	–	–	–	–	–	–

Similarly, facile formation of lactone **XVII** indicates *cis* arrangement of the reacting groups in **XVI** [scheme (1)] relative to the ring plane. The large C^1H proton chemical shift in the ^1H NMR spectra of both acid **XVI** (2.09 ppm) and lactone **XVII** (2.06 ppm) suggests the absence of vicinal *cis* substituents. Hence, the major isomer of **XVI** is [(1*SR*,2*RS*,5*SR*)-5-methyl-2-isopropenylcyclopentyl]acetic acid.

The precursors of **XV** and **XVI** are cyclic organomagnesium compounds **VII** and **VIII**, which, in turn, are formed by the magnesium–ene reactions (3) and (4) from open-chain Grignard reagents **V** and **VI**. Such a cyclization, often going to completion in ether, is suppressed in THF [4], and in this case after carboxylation we obtain acids **XIII** and **XIV**.

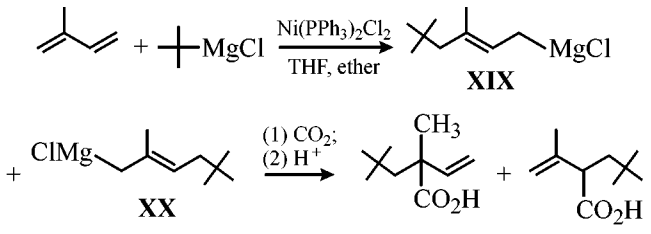


V **VII** (3)



VI **VIII** (4)

The ratio and yields of hydromagnesiation products **IX**–**XVI** strongly depend on the initial Grignard reagent, solvent, and catalyst (Tables 2, 3). With methylmagnesium halide containing no β-H atoms, no diene conversion is observed. Acids **IX** and **X** are formed only in minor amounts when the reaction is performed in the presence of $Ni(PPh_3)_2Cl_2$ catalyst (in THF better than in ether), but their amount becomes noticeable in the presence of $NiPy_4Cl_2$; in the latter case, acids **IX** and **X** are the only products when the reaction is performed in ether. Replacement of ether by THF in reactions performed in the presence of $Ni(PPh_3)_2Cl_2$ results in regular decrease in the yield of cyclic acids **XV** and **XVI** due to the lower cyclization rate. With bromides RMgBr used instead of chlorides RMgCl, the carboxylation products $H(C_5H_8)_2CO_2H$ are formed in lower yields or are not formed at all (with R = *s*-Bu). Still lower yields are obtained with RMgI. The influence of the alkyl radical in RMgX on the yields of acids **IX**–**XVI** is complex. *tert*-Butylmagnesium chloride in reaction with isoprene does not form hydromagnesiation products but forms 1,4- and 4,1-addition products [reaction (5)] in low yield. Trace amounts of such products are formed in the absence of the catalyst also.



XIX **XX** **XXI** **XXII** (5)

Table 4. Yields of products of isoprene hydromagnesiation in the presence of different catalysts (isoprene : *i*-PrMgCl/THF 1 : 1, 48 h, 18–20°C, 1 mol % catalyst)

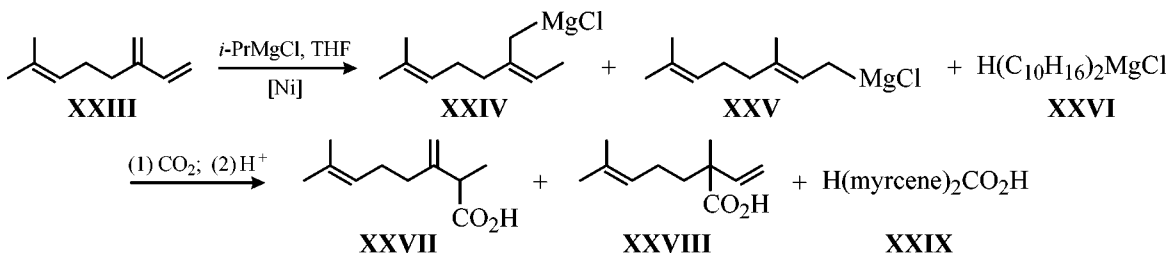
Run no.	Catalyst	**IX** + **X** (**IX**/**X**)	Σ Acids	Content of indicated $H(C_5H_8)_2CO_2H$ isomer, %					
				XI	**XII**	**XIII**	**XIV**	**XV**	**XVI**
1	$Ni(PPh_3)_2Cl_2$	6 (2.5 : 1)	41	40	17	18	7	4	4
2	$NiCl_2$	28 (2.5 : 1)	5						
3	$NiCl_2 + 2PPh_3$	1 (1 : 1)	28	40	17	25	6	3	3
4	$NiCl_2 + 2AsPh_3$	21 (3 : 1)	8	15	5	35	5	10	3
5	$NiCl_2 + 2SbPh_3$	6 (2 : 1)	24	21	13	36	6	9	5
6	$NiCl_2 + 2BiPh_3$	22 (3 : 1)	6	17	10	41	7	9	3
7	$Ni(PPh_2Pr)_2Cl_2$	–	20	38	17	20	9	3	3
8	$Ni(PPhPr_2)_2Cl_2$	–	5						
9	$Ni(PBu_3)_2Br_2$	–	<4						
10	$Ni[(p\text{-}CH_3\text{–}C_6H_4)_3P]_2Cl_2$	3 (1 : 1)	40						
11	$Ni(dppe)Cl_2$	20 (2 : 1)	5	9	5	27	5	34	Traces
12	$Ni[P(OPh)_3]_4$	–	–	–	–	–	–	–	–
13	$Ni[P(OEt)_3]_4$	–	–	–	–	–	–	–	–
14	$Ni[P(OCH_2Ph)_3]_2Br_2$	–	–	–	–	–	–	–	–
15	$Ni(COD)_2$	11 (2 : 1)	5	14	5	45	5	12	4
16	$NiCP_2$	28 (3 : 1)	5	25	10	25	5	10	Traces
17	$NiPy_4Cl_2$	17 (3 : 1)	12	10	5	40	5	Traces	″
18	$Ni(\alpha\text{-dipy})Cl_2$	25 (3 : 1)	6						
19	$Ni(acac)_2$	13 (3.5 : 1)	5						

The influence of the nickel complex on the course of isoprene hydromagnesiation is illustrated by data in Table 4. It is seen that nickel phosphite complexes (run nos. 12–14) do not catalyze the reaction. Regular increase in the donor power of the phosphine ligand on replacing aryl groups by alkyl groups (run nos. 1, 7–9) seem to result in a regular decrease in the yield of the reaction products. However, with $Ni[(p\text{-}CH_3C_6H_4)_3P]_2Cl_2$ (run no. 10), in which the ligand basicity is intermediate between those of PPh_2Pr and $PPhPr_2$ [7], the yields of the hydromagnesiation products are similar to those obtained with $Ni(PPh_3)_2Cl_2$. Thus,the catalyst activity increases with increasing number of aryl substituents in the ligand. Presumably, the course of the catalytic process is influenced by the configuration of the nickel complex: With decreasing number of aryl substituents in the phosphine the structure of the complex changes from tetrahedral (with PAr_3) to planar (with $PAlk_3$) [7].

Variation of the central atom in ligands EPh_3 (run nos. 3–6) shows that with weakly coordinating $AsPh_3$ and $BiPh_3$ the yield of $H(diene)_1CO_2H$ acids is higher than with PPh_3 and $SbPh_3$. A similar pattern was observed in hydromagnesiation of piperylene [6].

We also tested as isoprene hydromagnesiation catalysts some other transition metal complexes. With $Fe(acac)_2$, $Fe(acac)_3$, $Co(PPh_3O)_2Cl_2$, $Cu(\alpha\text{-dipy})_2Cl_2$, and $Pt(PPh_3)_2Cl_2$ no diene conversion was observed, and with $Cr(acac)_3$, $Pd(PPh_3)_2Cl_2$, $(PhCN)_2PdCl_2$, and $Rh(PPh_3)_3Cl$ the conversion was insignificant.

The influence of the chain length in the primary substituent in 2-substituted butadiene was examined with myrcene **XXIII** as example. 7-Methyl-3-methylene-1,6-octadiene **XXIII** proved to be considerably less active in hydrmagnesiation (6) with *i*-PrMgCl–THF–$Ni(PPh_3)_2Cl_2$, giving after carboxylation only a ~2 : 1 mixture of acids **XXVII** and **XXVIII** in a 5% yield and traces of telomeric acid **XXIX**:



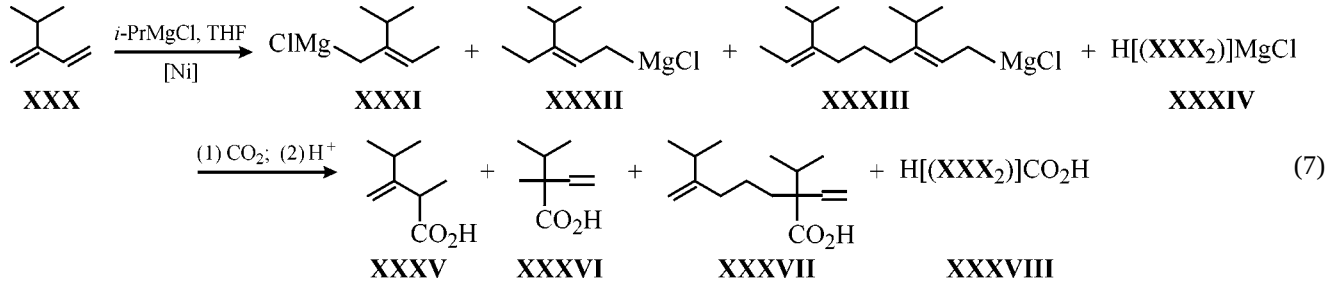
XXIII **XXIV** **XXV** **XXVI** **XXVII** **XXVIII** **XXIX** (6)

With $NiPy_4Cl_2$ as catalyst, the yield of acids (**XXVII**/**XXVIII**, 70 : 30) increases to 16%, and telodimerization products **XXIX** (~12%) are formed as a nondistillable (at 1 mm Hg) residue. Owing to the large difference between the content of acids **XXVII** and **XXVIII**, the ^{13}C and ^{1}H NMR signals could be assigned to particular isomers. For accurate assignment, we used data of [8–10].

Thus, as the length of the primary substituent in 2-substituted butadiene is increased, the number of hydromagnesiation products formed in the presence of $Ni(PPh_3)_2Cl_2$ decreases; in the presence of $NiPy_4Cl_2$, the compounds $H(diene)_1MgX$ and $H(diene)_2MgX$ are formed.

With 2-isopropylbutadiene **XXX** as example, we studied the effect exerted on hydromagnesiation [scheme (7)] by branching in the α-position of the alkyl substituent in 2-alkyl-substituted butadienes.

Reaction (7) is considerably slower than hydromagnesiation of isoprene. For example, from the reaction performed for 24 h in the presence of $NiPy_4Cl_2$, we isolated only acids **XXXV** and **XXXVI** (~1.5 : 1 ratio) in a low (3%) yield. The prolonged (100 h) reaction gave a higher (17%) yield of **XXXV** and **XXXVI** (~1 : 1 ratio), and additionally a mixture of telodimers $H[(\mathbf{XXX})_2]CO_2H$ was obtained in 15% yield, with 3,7-diisopropyl-1,7-octadiene-3-carboxylic acid **XXXVII** prevailing. When reaction (7) was performed with $Ni(PPh_3)_2Cl_2$ as catalyst, in 24 h we obtained only traces of unsaturated acids, and in 100 h we isolated, along with a mixture of **XXXV** and **XXXVI** (~1.5 : 1 ratio, yield 2%), also telodimer **XXXVII** (yield 19%) containing a ~20% impurity of other telodimers **XXXVIII**.

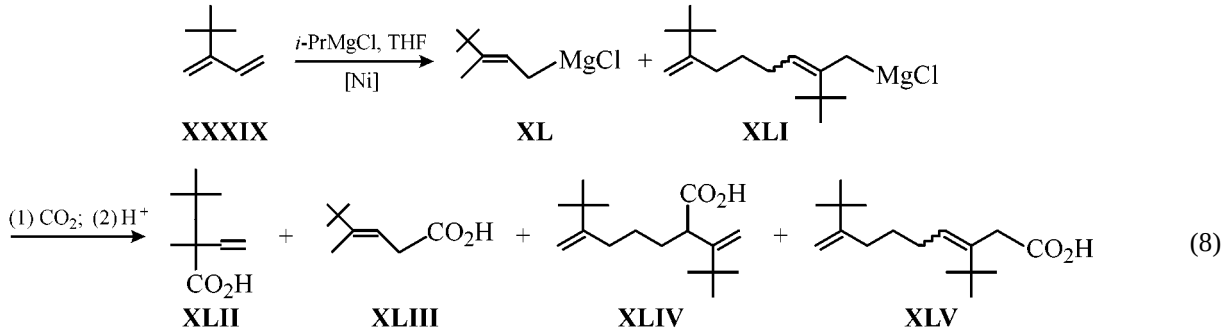


XXX **XXXI** **XXXII** **XXXIII** **XXXIV**

XXXV **XXXVI** **XXXVII** **XXXVIII**

(7)

With 2-*tert*-butylbutadiene **XXXIX**, in which the steric hindrance is still stronger, we obtained no noticeable amounts of hydromagnesiation products [reaction (8)] in the presence of $Ni(PPh_3)_2Cl_2$, and in the presence of $NiPy_4Cl_2$ allylic organomagnesium compounds **XL** and **XLI** were obtained.



XXXIX **XL** **XLI**

XLII **XLIII** **XLIV** **XLV**

(8)

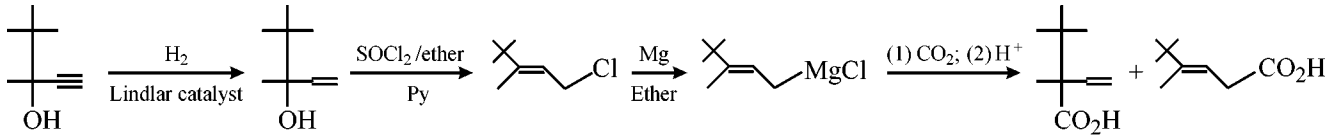
As the volume of the alkyl substituent increased in going from isoprene to myrcene, 2-isopropylbutadiene, and 2-*tert*-butylbutadiene, the ratio of the 4,1- and 1,4-hydromagnesiation products decreased, and from **XXXIX** we obtained isomer **XL** only.

However, in the NMR spectra of the fraction of $H[(\mathbf{XXXIX})_1]CO_2H$ acids we observed, along with signals of **XLII**, also the second sets of ^{1}H and ^{13}C signals, inconsistent with the structure of 2-methyl-3-*tert*-butyl-3-butenoic acid. We suggested that the

steric hindrance in 3,4,4-trimethyl-2-pentenylmagnesium chloride **XL** prevents complete rearrangement in the reaction with CO_2, so that the α-product, 4,5,5-trimethyl-3-hexenoic acid **XLIII**, is partially formed.

It is known that allylmagnesium halides react with sterically hindered di-*tert*-butyl ketone without rearrangement [11]. Furthermore, structurally related 4,4-dimethyl-2-pentenylmagnesium halide reacts with ketones to give a significant amount of the crotyl compound in a mixture with the usual γ-product [12].

By independent synthesis (9), we prepared 3,4,4-trimethyl-2-pentenylmagnesium chloride **XL**, which after carboxylation gave, indeed, the α-product **XLIII** along with the γ-product **XLII**.



XL **XLII** **XLIII**

(9)

The fraction of H[(**XXXIX**)$_2$]CO_2H acids contains, along with major isomer **XLIV**, also an impurity acid identified by ^1H and ^{13}C NMR spectroscopy as 3,8-di-*tert*-butyl-3,8-nonadienoic acid **XLV**. Here, also, the steric hindrance produced by the *tert*-butyl substituent in **XLI** prevents complete allyl rearrangement in the carboxylation stage. 2,7-Di-*tert*-butyl-1,7-octadiene-3-carboxylic acid **XLIV** can be readily separated from the impurity of **XLV** by recrystallization from aqueous methanol.

Thus, as the size of the alkyl substituent in 2-alkylbutadienes is increased, their hydromagnesiation involving both studied catalysts, $Ni(PPh_3)_2Cl_2$ and $NiPy_4Cl_2$, becomes more difficult, but the reaction selectivity increases. The reaction yields allylic organomagnesium compounds of the types H(diene)$_1$MgX and H(diene)$_2$MgX. The monomeric species are formed by 1,4- and 4,1-addition of [HMgX] to the diene molecule, with the ratio of the 4,1- and 1,4-addition products decreasing as the size of the alkyl substituent is increased. In the structure of the telodimers, one diene unit forms a bond "from the inside to the outside" via one of the double bonds, and the other diene unit is subject to conjugated addition, mostly by the 1,4 scheme. Only in the presence of the bulky *tert*-butyl group the addition to the second unit follows exclusively the 4,1 scheme.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrophotometer from 5% solutions in CCl_4 (layer thickness 250 μm). The NMR spectra were taken with a Bruker AC-500 spectrometer (500 MHz, 20–30 vol % solutions in $CDCl_3$, internal reference HMDS).

Grignard reagents were prepared under argon. Their solutions were filtered through glass wool and stored in Schlenk vessels. The Grignard reagents were used as 2.0–2.5 N solutions; the solutions of RMgBr in THF had a lower concentration, 0.9–1.0 N, because of the limited solubility. The solution concentration was determined by back-titration with alkali.

The nickel complexes were obtained by published procedures. Isoprene was dried over CaH_2 and distilled under argon; technical-grade myrcene was used.

2-Isopropyl-1,3-butadiene XXX. The precursor, 3,4-dimethyl-1-pentyn-3-ol, was prepared by the Favorskii reaction. A 2-l vessel equipped with a high-power Hershberg stirrer, a reflux condenser, a dropping funnel, and a gas-feeding tube was charged with 350 g of granulated KOH and 300 ml of absolute ether. The vessel was cooled with a water–ice mixture, and a stream of purified acetylene was passed to saturation. Then, a solution of 134 g of methyl isopropyl ketone (prepared from *tert*-amyl alcohol [13]) in 600 ml of absolute ether was added dropwise over a period of 4 h, with acetylene bubbling (~5 bubbles per second) and cooling being continued, after which the mixture was stirred for an additional 1 h in an acetylene stream and left overnight. After that, the reaction mixture was decomposed with ice at cooling, the organic layer was separated, and the aqueous layer was extracted with ether (2 × 100 ml). The combined organic phases were dried over K_2CO_3, the solvent was evaporated, and the residue was distilled. The following fractions were obtained: the first fraction, 5.0 g, bp 30–60°C (70 mm Hg), a mixture of unchanged methyl isopropyl ketone and 3,4-dimethyl-1-pentyn-3-ol, ~1 : 1; the second fraction, 75.8 g, bp 60–100°C (70 mm Hg), mainly 3,4-dimethyl-1-pen-

tyn-3-ol; and the residue, 48.0 g, crystallizing on cooling. Recrystallization of the residue from hexane gave 22.0 g of pure 2,7-dimethyl-4-octyne-3,6-diol, bp 74–75°C. ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.98 d and 1.02 d (12H, 4CH_3, *J* 6.8 Hz), 1.43 s (6H, CH_3C^3 and CH_3C^6), 1.79 septet (2H, C^2H and C^7H, *J* 6.8 Hz), 2.43 br.s and 2.46 br.s (2H, 2OH). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 17.5 and 17.8 (4CH_3), 27.3 (CH_3C^3 and CH_3C^6), 38.8 (C^2 and C^7), 71.5 (C^3 and C^6), 86.7 (C^4 and C^5).

Repeated fractionation of the combined first and second fractions gave 69.0 g of 3,4-dimethyl-1-pentyn-3-ol (yield 40%), bp 132–137°C. Published data: bp 134–134.5°C [14]. ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.99 d (3H, C^5H_3, $J_{5,4}$ 6.3 Hz), 1.03 d (3H, CH_3C^4, *J* 7.3 Hz), 1.44 s (3H, CH_3C^3), 1.80 septet (1H, C^4H, *J* ~6.8 Hz), 2.40 br.s (1H, OH), 2.42 s (1H, C^1H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 17.2 and 17.6 (2CH_3), 27.0 (CH_3C^3), 38.6 (C^4), 71.4 (C^3), 71.8 (C^1), 86.8 (C^2).

The resulting acetylenic alcohol (69.0 g) was hydrogenated at atmospheric pressure in 100 ml of cyclohexane in the presence of 10.4 g of Lindlar catalyst without adding quinoline for 24 h. After uptake of the calculated amount of hydrogen (~15 l), the filtered solution was distilled with a dephlegmator; the fraction boiling at 130–135°C (3,4-dimethyl-1-penten-3-ol) was collected. Yield 65.0 g (93%). Published data: bp 131°C [14]. ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.89 two d (6H, 2CH_3, *J* 6.8 Hz), 1.21 s (3H, CH_3C^3), 1.68 septet (1H, C^4H, *J* 6.8 Hz), 2.08 br.s (1H, OH), 5.03 d (1H, C^1HH, $J_{1,2}$ 10.6 Hz), 5.20 d (1H, C^1HH, *J* 17.3 Hz), 5.89 d.d (1H, C^2H, $J_{2,1}$ 10.6, 17.3 Hz).

The resulting 3,4-dimethyl-1-penten-3-ol (65 g) was dehydrated by dropping onto $KHSO_4$ at ~200°C, with simultaneous distillation of the products. The alcohol dropping rate was adjusted so as to keep the vapor temperature within 100°C [15]. The distillate was washed with water (2 × 50 ml) and dried over $CaCl_2$. The resulting product (51.0 g) was distilled; the fraction boiling below 120°C (28.8 g) was collected. After additional drying over $CaCl_2$, this product was fractionated. The following fractions were obtained: the first fraction, 13.1 g, bp 85–87°C, 2-isopropylbutadiene, purity ~90% (yield 22%, bp 86–87°C [14]); the second fraction, 11.8 g (16%), bp 90–110°C, a mixture of 2,3-dimethyl-1,3-pentadiene and 3,4-dimethyl-1,3-pentadiene, ~1 : 1, purity ~75%; and the residue, 2.5 g, mainly unchanged unsaturated alcohol. ^{1}H NMR spectrum of 2-isopropylbutadiene (500 MHz), δ, ppm: 1.08 d (6H, 2CH_3, *J* 6.6 Hz), 2.59 septet (1H, CHC^2, *J* 6.6 Hz), 4.96 s and 4.98 s (1H and 1H, C^1HH), 5.03 d (1H, C^4HH, $J_{4,3}$ 10.9 Hz), 5.26 d (1H, C^4HH, $J_{4,3}$ 17.5 Hz), 6.32 d.d (1H, C^3H, $J_{3,4}$ 10.9, 17.5 Hz). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 22.1 (2CH_3), 28.6 (CHC^2), 112.2 (C^1), 112.6 (C^4), 138.7 (C^3), 152.9 (C^2). ^{1}H NMR spectrum of 2,3-dimethyl-1,3-pentadiene (500 MHz), δ, ppm: 1.72 d (3H, C^5H_3, $J_{5,4}$ 7.0 Hz), 1.74–1.89 (2CH_3), 4.84 s and 4.95 s (C^1HH), 5.68 q (1H, C^4H, $J_{4,5}$ 6.8 Hz). ^{1}H NMR spectrum of 3,4-dimethyl-1,3-pentadiene (500 MHz), δ, ppm: 1.74–1.89 (3CH_3), 4.95 d (C^1HH), 5.07 d (C^1HH, $J_{1,2}$ 17.3 Hz), 6.83 d.d (C^2H, $J_{2,1}$ 10.9, 17.3 Hz).

2-*tert*-Butyl-1,3-butadiene was prepared according to [16]; its constants agreed with published data.

Hydromagnesiation of 2-alkylbutadienes (general procedure). A one-necked flask purged with argon (the presence of air, however, does not decrease the yield) was charged with 0.01 equiv of a catalyst and 1.0 equiv of a diene. The mixture was cooled with ice, and 1.1 equiv of a solution of alkylmagnesium halide was added, after which the mixture was allowed to warm up to room temperature. Then the flask was equipped with a hydroseal filled with silicone oil. The mixture was kept for 40–48 h at 20°C with intermittent shaking. Then the mixture was poured onto excess of crushed dry ice with stirring. After the mixture became liquid, ice and a saturated aqueous solution of oxalic acid were added to acidic reaction, avoiding self-heating (acidification with dilute HCl results in partial isomerization of the methylene double bond into an internal double bond). The mixture was extracted with two portions of ether. The combined extract was shaken with an excess of 10% NaOH. The alkaline aqueous layer was separated and washed with ether. Then the alkaline aqueous solution was cooled with ice and acidified with a saturated oxalic acid solution; the released carboxylic acids were extracted with ether. The combined ether extracts were dried over $MgSO_4$, the solvent was evaporated, and the residue was vacuum-distilled.

Below we give an example of fractionating the mixture of carboxylic acids obtained from carboxylation of the system isoprene (3.4 g)–*i*-PrMgCl–THF–$Ni(PPh_3)_2Cl_2$: the first fraction, 1.7 g, bp 70–85°C (20 mm Hg), isobutyric acid, traces of butyric acid, 7% impurity of acids **IX** and **X**; the second fraction, 0.4 g, bp 100–105°C (20 mm Hg), mixture of acids **IX** and **X**, 2.5 : 1; the third fraction, 1.9 g, bp 145–155°C (20 mm Hg), mixture of acids **XI** (40%), **XII**

(17%), **XIII** (18%), **XIV** (7%), **XV** (4%), and **XVI** (4%). The yields of the compounds from the reactions with isoprene are listed in Tables 2–4. ^{1}H NMR spectrum of **2,3-dimethyl-3-butenoic acid IX** (without its isolation; 80 MHz), δ, ppm: 1.30 d (3H, CH_3C^2, *J* 7.0 Hz), 1.82 s (3H, CH_3C^3), 3.10 q (1H, C^2H, *J* 7.0 Hz), 4.87 s (2H, C^4H_2), 12.5 br.s (1H, CO_2H). ^{13}C NMR spectrum (50 MHz), δ_C, ppm: 15.3 (CH_3C^2), 20.1 (CH_3C^3), 46.5 (C^2), 112.9 (C^4), 143.1 (C^3), 181.0 (C^1).

^{1}H NMR spectrum of **2,2-dimethyl-3-butenoic acid X** (without its isolation; 80 MHz), δ, ppm: 1.32 s (6H, $2CH_3$), 5.04 d.d (1H, C^4HH, *J* 10.5, 1 Hz), 5.09 d.d (1H, C^4HH, *J* 17.5, 1 Hz), 6.03 d.d (1H, C^3H, *J* 10.5, 17.5 Hz), 12.5 br.s (CO_2H). ^{13}C NMR spectrum (50 MHz), δ_C, ppm: 24.3 ($2CH_3$), 44.6 (C^2), 113.2 (C^4), 141.9 (C^3), 183.2 (C^1).

^{1}H NMR spectrum of **3,7-dimethyl-1,7-octadiene-3-carboxylic acid XI** (500 MHz), δ, ppm: 1.27 s (CH_3C^3), 1.41 m (C^5H_2), 1.56 m and 1.70 m (C^4H_2), 1.66 s (CH_3C^7), 1.98 t (C^6H_2, *J* 7.2 Hz), 4.64 s and 4.68 s (C^8H_2), 5.10 d (C^1HH, *J* 11.0 Hz), 5.11 d (C^1HH, *J* 17.7 Hz), 6.01 d.d (C^2H, *J* 17.7, 11.0 Hz), 11.9 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 20.1 (CH_3C^3), 21.9 (CH_3C^7), 22.1 (C^5), 37.8 (C^6), 38.3 (C^4), 48.2 (C^3), 110.2 (C^8), 113.8 (C^1), 140.9 (C^2), 144.8 (C^7), 182.6 (CO_2H).

^{1}H NMR spectrum of **2,7-dimethyl-1,7-octadiene-3-carboxylic acid XII** (500 MHz), δ, ppm: 1.41 m (C^5H_2), 1.57 m and 1.76 m (C^4H_2), 1.67 s (CH_3C^7), 1.75 s (CH_3C^2), 2.00 m (C^6H_2), 3.03 t (C^3H, *J* 7.5 Hz), 4.90 s (C^1H_2), 4.64 s and 4.68 s (C^8H_2), 11.9 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 19.8 (CH_3C^2), 21.9 (CH_3C^7), 25.1 (C^5), 29.3 (C^4), 37.3 (C^6), 52.8 (C^3), 110.2 (C^8), 114.3 (C^1), 141.7 (C^2), 144.8 (C^7), 180.2 (CO_2H).

^{1}H NMR spectrum of **3,6-dimethyl-1,7-octadiene-3-carboxylic acid XIII** (without its isolation; 500 MHz), δ, ppm: 0.98 d (CH_3C^6, *J* 7 Hz), 1.26 s (CH_3C^3), 1.4–2.2 m (C^4H_2 + C^5H_2 + C^6H_2), 4.9–5.0 m (C^8H_2), 5.10 d.d (C^1H_2), 5.65 m (C^7H), 6.00 d.d (C^2H, *J* 18 and 11 Hz), 12 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 20.0 (CH_3C^6), 20.1 (CH_3C^3), 31.0 (C^5), 36.5 (C^4), 38.0 (C^6), 48.2 (C^3), 112.9 (C^8), 113.9 (C^1), 140.9 (C^2), 144.0 (C^7), 182.5 (CO_2H).

^{1}H NMR spectrum of **2,6-dimethyl-1,7-octadiene-3-carboxylic acid XIV** (without its isolation; 500 MHz), δ, ppm: 0.98 d (CH_3C^6), 1.4–2.2 m (C^4H_2 + C^5H_2 + C^6H_2), 1.75 s (CH_3C^2), 3.00 t (C^3H, *J* 7.6 Hz), 4.9 s (C^1H_2), 4.9–5.0 m (C^8H_2), 5.65 m (C^7H), 12 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 19.8 (CH_3C^6), 19.9 (CH_3C^2), 27.5 (C^5), 34.1 (C^4), 37.7 (C^6), 53.0 (C^3), 113.0 (C^8), 144.4 (C^1), 141.8 (C^2), 143.9 (C^7), 180.3 (CO_2H).

2-(2,5-Dimethyl-2-vinylcyclopentyl)acetic acid XV and **2-(5-methyl-2-isopropenylcyclopentyl)acetic acid XVI.** A mixture of 27.2 g of isoprene, 250 mmol of *i*-PrMgCl in ether, and 1.3 g of $Ni(PPh_3)_2Cl_2$ was allowed to stand at room temperature for 24 h. Then 35 ml of Me_3SiCl was added with cooling, and the mixture was allowed to stand for an additional 24 h. The resulting mixture was poured onto an excess of crushed dry ice and worked up as described above (with oxalic acid). After distilling off isobutyric acid [bp ~93°C (80 mm Hg)], 3 ml of water was added to the residue, and the remaining traces of butyric acids were steam-distilled. The residue was fractionated; the fraction with bp 132–134°C (4 mm Hg) was collected (2.8 g, mixture of acids **XV** and **XVI**, ~1 : 1, yield 8%). Found, %: C 72.31; H 10.20. $C_{11}H_{18}O_2$. Calculated, %: C 72.49; H 9.95. The NMR spectra are given in Table 1. The major (~90%) isomers in the products are **[(1*SR*,2*SR*,5*SR*)-2,5-dimethyl-2-vinylcyclopentyl]acetic acid and 2-[(1*SR*,2*RS*,5*SR*)-5-methyl-2-isopropenylcyclopentyl]acetic acid**, respectively.

2-(2,5-Dimethyl-2-vinylcyclopentyl)acetic acid XV and **(4a*SR*,5*SR*,7a*RS*)-1,1,5-trimethylperhydrocyclopenta[*c*]pyran-3-one XVII.** A 40% aqueous solution of HBr (7 ml) was added to 1.7 g of the obtained mixture of acids **XV** and **XVI**. The mixture was shaken on a rocker at room temperature for 10 h, after which it was extracted with pentane (2 × 10 ml). The extract was washed with 10 ml of water and dried over $MgSO_4$; the solvent was evaporated. The residue was a ~1 : 1 mixture of **XV** and **XVII**. This residue was dissolved in 10 ml of 5 M NaOH; the solution was extracted with pentane (2 × 10 ml). The extract was dried over $MgSO_4$, evaporated, and distilled [bp 91–92°C (1–2 mm Hg)] to give 0.7 g (82%) of lactone **XVII**. The alkaline solution was acidified with 10% HCl and extracted with pentane (2 × 10 ml). The extract was dried over $MgSO_4$, evaporated, and distilled to give 0.7 g (82%) of pure acid **XV**, bp 97–98°C (1 mm Hg). Compound **XVII**. IR spectrum, ν, cm^{-1}: 2940, 2865, 1750, 1440, 1405, 1370, 1290, 1255, 1223, 1184, 1155, 1130, 970, 950, 930, 908. ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.96 s (3H, CH_3C^9-*exo*), 0.96 d (3H, CH_3C^9-*endo*, *J* 13.4 Hz),

1.01 d (3H, CH_3C^5, $J_{6,5}$ 5.9 Hz), 1.24 m and 1.85 m (C^4H_2), 1.79 m (C^5H), 1.83 m (C^2H), 1.86 m and 2.01 m (C^3H_2), 2.06 m (C^1H), 2.30 d (1H, C*H*HCO$_2$, *J* 18.5 Hz), 2.75 d.d (1H, CH*H*CO$_2$, *J* 9.6, 18.5 Hz). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 16.8 (CH_3C^9-*exo*), 17.2 (CH_3C^9-*endo*), 18.8 (CH_3C^5), 32.3 (C^4), 34.3 (C^3), 35.75 (C^2), 35.78 (C^7), 42.1 (C^5), 48.1 (C^1), 100.7 (C^9), 176.9 (CO_2). Found, %: C 72.15; H 10.18. $C_{11}H_{18}O_2$. Calculated, %: C 72.49; H 9.95. Compound **XV**. IR spectrum, ν, cm^{-1}: 3400–2400 br, 1755, 1685, 1620, 1440, 1395, 1370, 1290, 1228, 1180, 910. Acid **XVI** does not react with concentrated HCl solutions at room temperature.

(4a*SR*,5*SR*,7a*RS*)-1-Iodomethyl-5,7a-dimethylperhydrocyclopenta[*c*]pyran-3-one XVIII. A solution of 0.4 g of **XV** in 10 ml of 5% $NaHCO_3$ was added dropwise with stirring at 20°C to a solution of 0.65 g of KI and 1.0 g of I_2 in 5 ml of H_2O. The mixture was stirred for 15 min and extracted with ether (2×15 ml); the extract was washed with a dilute Na_2SO_3 solution and dried over $MgSO_4$. The solvent was vacuum-evaporated. The residue crystallized (0.55 g, mainly **XVIII**, yield 81%). ^1H NMR spectrum of the major isomer, **XVIII** (500 MHz), δ, ppm: 0.97 s (3H, CH_3C^{7a}), 1.05 d (3H, CH_3C^5, *J* 6.4 Hz), 1.31–1.43 m (2H), 1.51 m (1H), 1.55–1.68 m (2H), 1.82 m (1H), 2.21 d.d (1H, C^4*H*H, $J_{4,4}$ 14.6, $J_{4,4a}$ 11.1 Hz), 2.70 d.d (1H, C^{4}H*H*, $J_{4,4}$ 14.6, $J_{4,4a}$ 6.2 Hz), 3.21–3.32 m (2H, CH_2I), 4.21 m (1H, C^1H). ^{13}C NMR spectrum of the major isomer, **XVIII** (125 MHz), δ_C, ppm: 1.4 (CH_2I), 18.1 (CH_3), 21.3 (CH_3), 33.7 (CH_2), 34.3 (CH_2), 36.9 (CH_2), 44.4 (CH), 46.5 (C^{7a}), 52.0 (CH), 85.6 (C^1H), 172.2 (C^3).

Reaction of isoprene with *tert*-butylmagnesium chloride. From 50 mmol of isoprene, 55 mmol of *t*-BuMgCl in THF, and 0.5 mmol of $Ni(PPh_3)_2Cl_2$, the following fractions were obtained after distillation: the first fraction, 1.8 g, bp 88°C (40 mm Hg), 2,2-dimethylpropanoic acid; the residue, 0.3 g of a liquid, a mixture of ~50% of 2,2-dimethylpropanoic acid and ~50% of 2-methyl-2-neopentyl-3-butenoic acid **XXI** and 3-methyl-2-neopentyl-3-butenoic acid **XXII** (~5 : 1, yield 2%). ^1H NMR spectrum of **XXI** (500 MHz), δ, ppm: 0.95 s [9H, $(CH_3)_3C$], 1.37 s (3H, CH_3C^2), 1.66 d and 1.85 d (1H and 1H, CH_2C^2, J_{gem} 14.3 Hz), 5.06 d (1H, C^4*H*H, $J_{4,3}$ 10.8 Hz), 5.10 d (1H, C^{4}H*H*, $J_{4,3}$ 17.5 Hz), 6.10 d.d (1H, C^3H, $J_{3,4}$ 10.8, 17.5 Hz), 11.5 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 22.2 (CH_3C^2), 31.0 [$(CH_3)_3C$], 31.8 [$(CH_3)_3C$], 48.2 (CH_2C^2), 52.6 (C^2), 112.8 (C^4), 142.8 (C^3), 183.3 (C^1O_2H). To compound **XXII** in the ^1H NMR spectrum of the mixture correspond the signals at δ 4.85 and 4.93 ppm, s (C^4H_2), and in the ^{13}C NMR spectrum, the signals at δ_C 113.3 (C^4), 143.7 (C^3), and 180.8 ppm (C^1).

Hydromagnesiation of myrcene XXIII. From 8.5 g of myrcene (75% content), 55 mmol of *i*-PrMgCl in THF, and 0.327 g of $Ni(PPh_3)_2Cl_2$, the following fractions were obtained after distillation: the first fraction, 2.5 g, bp 100–102°C (160 mm Hg), a mixture of 91% of isobutyric acid (traces of $PrCO_2H$) and 9% of 2,7-dimethyl-3-methylene-6-octenoic acid **XXVII** + 3,7-dimethyl-1,6-octadiene-3-carboxylic acid **XXVIII**, ~2 : 1; residue, 0.2 g. Yield of **XXVII** + **XXVIII** 5%.

From 8.5 g of myrcene (75% content), 55 mmol of *i*-PrMgCl in THF, and 0.242 g of $NiPy_4Cl_2$, the following fractions were obtained after distillation: the first fraction, 1.3 g, bp 100–105°C (110 mm Hg), a mixture of isobutyric (80%) and butyric (20%) acids; the second fraction, 1.5 g, bp 103–107°C (2 mm Hg), acids **XXVII** and **XXVIII** in a ~70 : 30 ratio, yield 16%; the residue, a dark viscous tar, nondistillable at 2 mm Hg (dec.), presumably H(myrcene)$_2CO_2H$. ^1H NMR spectrum of **XXVII** (500 MHz), δ, ppm: 1.28 d (CH_3C^2, *J* 7.0 Hz), 1.59 s (CH_3C^7), 1.66 s (C^8H_3), 2.0–2.15 m (C^4H_2 + C^5H_2), 3.14 q (C^2H, *J* 7.0 Hz), 4.92 s and 4.98 s ($CH_2=C^3$), 5.10 m (C^6H), 11.9 br.s (C^1O_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 15.9 (CH_3C^2), 17.5 (CH_3C^7), 25.5 (C^8), 26.3 (C^5), 34.6 (C^4), 45.5 (C^2), 111.3 ($CH_2=C^3$), 123.7 (C^6), 131.6 (C^7), 147.4 (C^3), 181.0 (CO_2H). ^1H NMR spectrum of **XXVIII** (500 MHz), δ, ppm: 1.28 s (CH_3C^3), 1.56 s (CH_3C^7), 1.64 s (C^8), 1.5–2.0 m (C^4H_2 + C^5H_2), 5.05–5.15 m (C^1H_2), 5.10 m (C^6H), 6.03 d.d (C^2H, $J_{1,2}$ 10.6, 17.6 Hz), 11.9 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 17.4 (CH_3C^7), 20.0 (CH_3C^3), 23.2 (C^5), 25.4 (C^8), 38.9 (C^4), 48.3 (C^3), 113.8 (C^1), 123.6 (C^6), 131.8 (C^7), 141.0 (C^2), 182.5 (CO_2H).

Hydromagnesiation of 2-isopropylbutadiene XXX. A mixture of 6.7 g of 2-isopropylbutadiene, 75 mmol of *i*-PrMgCl in THF, and 0.458 g of $Ni(PPh_3)_2Cl_2$ was allowed to stand for 24 h and worked up by a common procedure. The residue (0.2 g) after distilling off 2.9 g of isobutyric acid was a mixture of unsaturated acids.

A mixture of 7.2 g of 2-isopropylbutadiene, 100 mmol of *i*-PrMgCl in THF, and 0.621 g of $Ni(PPh_3)_2Cl_2$ was allowed to stand for 100 h and carboxylated as described above. The following frac-

tions were obtained after distillation: the first fraction, 0.8 g, bp 100°C (100 mm Hg), pure isobutyric acid; the second fraction, 0.3 g, bp 45–55°C (1–2 mm Hg), consisting to 80% of a mixture of 2-methyl-3-isopropyl-3-butenoic acid **XXXV** and 2-methyl-2-isopropyl-3-butenoic acid **XXXVI**, 1.5 : 1 (yield 2%); and the third fraction, 2.2 g, bp 136–142°C (3 mm Hg), **3,7-diisopropyl-1,7-octadiene-3-carboxylic acid XXXVII** (~80% in the mixture). ^{1}H NMR spectrum of acid **XXXV** (without its isolation; 500 MHz), δ, ppm: 1.05 d and 1.07 d [(C*H*$_3$)$_2$CH, *J* 6.8 Hz], 1.29 d (CH$_3$C^2, *J* 7.1 Hz), 2.34 septet [(CH$_3$)$_2$C*H*, *J* 6.8 Hz], 3.14 q (C^{2}H, *J* 7.1 Hz), 4.96 s and 4.98 s (C^{4}H$_2$), 12.0 br.s (C^{1}O$_2$H). ^{13}C NMR spectrum (125 MHz), δ$_C$, ppm: 17.3 (*C*H$_3$C^2), 21.8 and 22.0 [(*C*H$_3$)$_2$CH], 33.9 [(CH$_3$)$_2$*C*H], 43.7 (C^2), 109.0 (C^4), 154.5 (C^3), 181.6 (C^{1}O$_2$H).

^{1}H NMR spectrum of **XXXVI** (without its isolation; 500 MHz), δ, ppm: 0.84 d and 0.88 d [(C*H*$_3$)$_2$CH, *J* 6.8 Hz], 1.17 s (CH$_3$C^2), 2.15 septet [(CH$_3$)$_2$C*H*, *J* 6.8 Hz], 5.11 d (C^4*H*H, *J* 17.4 Hz), 5.17 d (C^{4}H*H*, *J* 11.6 Hz), 6.0 d.d (C^{3}H, $J_{3,4}$ 11.6, 17.4 Hz), 12.0 br.s (C^{1}O$_2$H). ^{13}C NMR spectrum (125 MHz), δ$_C$, ppm: 13.9 (*C*H$_3$C^2), 17.1 and 17.6 [(*C*H$_3$)$_2$CH], 34.5 [(CH$_3$)$_2$*C*H], 52.4 (C^2), 114.9 (C^4), 140.3 (C^3), 182.9 (C^{1}O$_2$H).

^{1}H NMR spectrum of acid **XXXVII** (500 MHz), δ, ppm: 0.83 d and 0.88 d [6H, (C*H*$_3$)$_2$CHC^3, *J* 7.0 Hz], 1.00 d [6H, (C*H*$_3$)$_2$CHC^7, *J* 6.8 Hz], 1.31 m and 1.48 m (C^{5}H$_2$), 1.71 m (C^{4}H$_2$), 2.02 m (C^{6}H$_2$), 2.08 septet [1H, (CH$_3$)$_2$C*H*C^3, *J* 7.0 Hz], 2.18 septet [1H, (CH$_3$)$_2$C*H*C^7, *J* 6.8 Hz], 4.64 s and 4.72 s (2H, C^{8}H$_2$), 5.04 d (1H, C^1*H*H, *J* 18.0 Hz), 5.28 d (1H, C^{1}H*H*, *J* 11.3 Hz), 6.01 d.d (1H, C^{2}H, *J* 11.3, 18.0 Hz), 11.5 br.s (CO$_2$H). ^{13}C NMR spectrum (125 MHz), δ$_C$, ppm: 16.8 and 18.6 [(*C*H$_3$)$_2$CHC^3], 21.8 [(*C*H$_3$)$_2$CHC^7], 23.2 (C^5), 33.4 (C^4), 33.5 [(CH$_3$)$_2$*C*HC^7], 34.8 (C^6), 35.4 (C^9), 56.2 (C^3), 106.6 (C^8), 115.8 (C^1), 135.2 (C^2), 155.2 (C^7), 182.5 (CO$_2$H).

A mixture of 5.1 g of 2-isopropylbutadiene, 60 mmol of *i*-PrMgCl in THF, and 0.257 g of NiPy$_4$Cl$_2$ was allowed to stand for 24 h, carboxylated, and distilled. The following fractions were obtained: the first fraction, 1.7 g, bp 75–90°C (40–35 mm Hg), isobutyric acid + 6% PrCO$_2$H; and the second fraction, 0.4 g, bp 74–80°C (3 mm Hg), consisting to 75% of a mixture of acids **XXXV** and **XXXVI**, 1.5 : 1 (yield 3%). A mixture of 9.1 g of 2-isopropylbutadiene, 100 mmol of *i*-PrMgCl in THF, and 0.46 g of NiPy$_4$Cl$_2$ was allowed to stand for 100 h, carboxylated, and distilled. The following fraction were obtained: the first fraction, 2.1 g, bp 69– 74°C (18 mm Hg), isobutyric acid + 6% PrCO$_2$H; the second fraction, 2.3 g, bp 122–124°C (18 mm Hg), a mixture of acids **XXXV** and **XXXVI**, 1 : 1 (yield 17%); the third fraction, 1.7 g, bp 133–-136°C (3 mm Hg), a mixture of telodimers consisting to more than 50% of acid **XXXVII** (total yield 15%); and the residue, 1.5 g of a dark tar.

Hydromagnesiation of 2-*tert*-butylbutadiene XXXIX. A mixture of 5.5 g of 2-*tert*-butylbutadiene, 55 mmol of *i*-PrMgCl in THF, and 0.327 g of Ni(PPh$_3$)$_2$Cl$_2$ was allowed to stand for 50 h, carboxylated, and distilled. The following fractions were obtained: the first fraction, 2.3 g, bp 100°C (100 mm Hg), isobutyric acid; the second fraction, 0.2 g (the ^{1}H NMR spectrum contains noticeable signals of vinyl protons).

A mixture of 5.3 g of 2-*tert*-butylbutadiene, 55 mmol of *i*-PrMgCl in THF, and 0.242 g of NiPy$_4$Cl$_2$ was allowed to stand for 50 h, carboxylated, and distilled. The following fractions were obtained: the first fraction, 1.8 g, bp 74–75°C (30 mm Hg), isobutyric acid containing 2% PrCO$_2$H; the second fraction, 0.1 g, bp 100–130°C (3 mm Hg), a mixture of acids **XLII** and **XLIII**; the third fraction, 1.0 g, bp 130–150°C (3 mm Hg), a mixture of acids **XLII**, **XLIII**, and **XLIV** + **XLV** in the ~20 : 20 : 60 ratio; the fourth fraction, 0.3 g, bp 150°C (3 mm Hg), a mixture of acids **XLIV** and **XLV**, ~5 : 1; and the residue, 0.8 g, a viscous tar. Total yield of acids **XLII** and **XLIII** (~1 : 1) 7%; total yield of acids **XLIV** and **XLV** (~5 : 1) 14%.

A 0.1-g portion of the viscous liquid from the fourth fraction was heated with 1 ml of water to ~80°C, and methanol was added dropwise until the mixture became homogeneous. The solution was left overnight in a refrigerator (–8°C), and the colorless crystals that formed were filtered off and dried in a desiccator. Pure **2,7-di-*tert*-butyl-1,7-octadiene-3-carboxylic acid XLIV** was obtained; mp 73–74°C. IR spectrum, ν, cm^{-1}: 3400–2400 br, 1695, 1620, 1470, 1450, 1400, 1360, 1280, 1230, 1200, 1158, 908, 890, 715. Found, %: C 76.32; H 11.41. C$_{17}$H$_{30}$O$_2$. Calculated, %: C 76.64; H 11.35.

^{1}H NMR spectrum of 2-methyl-2-*tert*-butyl-3-butenoic acid **XLII** (500 MHz), δ, ppm: 0.98 s [(CH$_3$)$_3$CC^2], 1.26 s (CH$_3$C^2), 5.07 d (C^4*H*H, $J_{4,3}$ 17.5 Hz), 5.16 d (C^{4}H*H*, $J_{4,3}$ 11.2 Hz), 6.31 d.d (C^{3}H, $J_{3,4}$ 11.2, 17.5 Hz), 10.5 br.s (C^{1}O$_2$H). ^{13}C NMR spectrum (125 MHz), δ$_C$, ppm: 15.7 (*C*H$_3$C^2), 26.3 [(*C*H$_3$)$_3$C], 36.1 [(CH$_3$)$_3$*C*], 54.1 (C^2), 114.4 (C^4), 139.2 (C^3), 181.9 (C^1).

^{1}H NMR spectrum of 4,5,5-trimethyl-3-hexenoic acid **XLIII** (500 MHz), δ, ppm: 1.04 s [$(CH_3)_3CC^4$], 1.63 s (CH_3C^4), 3.08 d (C^2H_2, $J_{2,3}$ 6.6 Hz), 5.39 t (C^3H, $J_{3,2}$ 6.6 Hz), 10.5 br.s (C^1O_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 13.1 (CH_3C^4), 28.8 [$(CH_3)_3C$], 33.7 (C^2), 36.3 [$(CH_3)_3C$], 112.0 (C^3), 147.3 (C^4), 179.2 (C^1).

^{1}H NMR spectrum of **XLIV** (500 MHz), δ, ppm: 1.03 s and 1.09 s [9H and 9H, $2(CH_3)_3C$], 1.41–1.59 m (C^5H_2 and C^4HH), 1.91 m (1H, C^4HH), 2.03 m (2H, C^6H_2), 3.12 d.d (1H, C^3H, $J_{3,4}$ 9.8, 3.8 Hz), 4.66 s and 4.84 s (2H, C^8H_2), 5.06 s and 5.07 s (2H, C^1H_2), 11.7 br.s (CO_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 27.7 (C^5), 28.7 and 29.3 [$2(CH_3)_3C$], 31.0 (C^4), 35.0 (C^6), 36.0 and 36.9 [$2(CH_3)_3C$], 46.3 (C^3), 105.8 (C^8), 109.3 (C^1), 155.6 (C^2), 157.5 (C^7), 180.8 (CO_2H).

^{1}H NMR spectrum of 3,8-di-*tert*-butyl-3,8-nonadienoic acid **XLV** (without its isolation; 500 MHz), δ, ppm: 1.03 s and 1.06 s [$2(CH_3)_3C$], 1.50–1.59 m (C^6H_2), 2.0–2.1 m (C^5H_2 + C^7H_2), 3.05–3.12 m (C^2H_2), 4.69 s and 4.87 s (C^9H_2), 5.45 m (C^4H), 11.7 br.s (C^1O_2H). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 28.5 (C^6), 28.7 and 29.3 [$2(CH_3)_3C$], 30.2 (C^5), 32.0 (C^7), 33.8 (C^2), 36.1 and 36.7 [$2(CH_3)_3C$], 106.3 (C^9), 113.3 (C^4), 151.2 (C^3), 157.2 (C^8), 179.1 (C^1O_2H).

Independent synthesis of 3,4,4-trimethyl-2-pentenylmagnesium chloride XL. A solution of 25.2 g of 3,4,4-trimethyl-1-pentyn-3-ol in 70 ml of cyclohexane was hydrogenated in the presence of 5 g of Lindlar catalyst and 1 g of quinoline until 4.8 l of hydrogen was taken up. The solution was filtered, and the solvent was distilled off at temperatures of up to 90°C. The residue was distilled, and the fraction boiling at 56°C (35 mm Hg) was collected. **3,4,4-Trimethyl-1-penten-3-ol**, yield 20.2 g (79%). ^{1}H NMR spectrum (500 MHz), δ, ppm: 0.93 s [9H, $(CH_3)_3C$], 1.23 s (3H, CH_3C^3), 5.08 d (1H, C^1HH, $J_{1,2}$ 11.1 Hz), 5.21 d (1H, C^1HH, $J_{1,2}$ 17.0 Hz), 6.07 d.d (1H, C^2H, $J_{2,1}$ 11.2, 17.0 Hz).

Thionyl chloride (19.3 g) was added dropwise with stirring and cooling with ice to a mixture of 20.0 g of 3,4,4-trimethyl-1-penten-3-ol and 12.6 g of pyridine in 70 ml of absolute ether. The resulting white suspension was allowed to stand for 2 h at 15–20°C and then decomposed by adding water until the precipitate completely dissolved. The ether layer was separated, washed with water (2 × 50 ml), and dried over $CaCl_2$. The solvent was evaporated, and the residue was distilled; the fraction boiling at 69–70°C (30 mm Hg) was collected. **3,4,4-Trimethyl-1-chloro-2-pentene**, yield 13.4 g (59%). ^{1}H NMR spectrum (500 MHz), δ, ppm: 1.04 s [9H, $(CH_3)_3C$], 1.71 s (3H, CH_3C^3), 4.10 d (2H, C^1H_2, $J_{1,2}$ 8.3 Hz), 5.50 t (1H, C^2H, $J_{2,1}$ 8.3 Hz). ^{13}C NMR spectrum (125 MHz), δ_C, ppm: 12.6 (CH_3C^3), 28.7 [$(CH_3)_3C$], 36.4 (C^4), 41.6 (C^1), 117.3 (C^2), 150.5 (C^3).

A solution of 6.5 g of 3,4,4-trimethyl-1-chloro-2-pentene in 20 ml of absolute THF was added dropwise with stirring and cooling with water to 2.4 g of Mg in 100 ml of absolute THF at a rate at which the mixture did not boil. The ready solution of Grignard reagent **XL** was decanted from excess magnesium and its salts and poured onto an excess of crushed dry ice. The mixture was acidified with an HCl solution and extracted with pentane (2 × 40 ml). The acids were transferred into an alkaline aqueous solution, which was then acidified and extracted with pentane (2 × 30 ml). The extract was evaporated, and the residue was distilled; bp 90–95°C (2 mm Hg), 1.0 g (14%), liquid solidifying in a refrigerator to give white crystals of a mixture of **3,4,4-trimethyl-1-pentene-3-carboxylic acid XLII** and **4,5,5-trimethyl-3-hexenoic acid XLIII** in a 68 : 32 ratio.

Carboxylation of a 1 : 2 mixture of organomagnesium compound **XL** and *i*-PrMgCl in THF yielded carboxylic acids **XLII** and **XLIII**, 57 : 43. Carboxylation of Grignard reagent **XL** prepared in ether yielded a mixture of acids **XLII** and **XLIII** in a 91 : 9 ratio.

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