$$k_p^{\text{trans}}[c^*]^{1/4}(1-\alpha)[M] = k_{\text{iso}}[c^*](\alpha-\alpha_0) \tag{A4}$$

or

$$\alpha = (1 + X\alpha_0)/(1 + X) \tag{A5}$$

where $X = k_{\text{iso}}[c^*]/k_p^{\text{trans}}[c^*]^{1/4}[M]$.

Now the fraction of trans units (f_{trans}) incorporated in the polymer will be given by the fraction of trans units adding monomer if trans centers alone incorporate their structure on monomer addition i.e.,

$$f_{\text{trans}} = k_p^{\text{trans}}(1-\alpha)/(k_p^{\text{trans}}(1-\alpha) + k_p^{\text{cis}}\alpha) \tag{A6}$$

Let the ratio $k_p^{\text{cis}}/k_p^{\text{trans}} = R$, then

$$f_{\text{trans}} = (1-\alpha)/(1 + \alpha(R-1)) \tag{A7}$$

Substitution of eq A5 in A7 gives

$$f_{\text{trans}} = \left[1 + \frac{R}{X}\left(\frac{1 + X\alpha_0}{1-\alpha_0}\right)\right]^{-1} \tag{A8}$$

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Magnesium-Assisted Stereospecific Oligomerization of Isoprene. Unique Chemical Behaviors of Magnesium–Isoprene Adducts, $[\mathrm{Mg(C_5H_8)}_m]_n$

Hajime Yasuda,* Yoshio Nakano, Kazuteru Natsukawa, and Hisaya Tani

Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received October 28, 1977*

ABSTRACT: The mechanism of the stepwise formation of oligomeric 3,4-polyisoprene with activated magnesium was studied. The oligomerization successively proceeded via the magnesium–isoprene 1:1 (**1**), 1:2 (**2**), 1:3 (**3**), and 1:4 (**4**) adducts. These adducts were isolated in a pure state and their macrocyclic structures were confirmed by the measurement of the molecular weight and by NMR spectroscopy. Based on the geometry of the isoprene moiety of adducts **1–4**, the process of initiation in the oligomerization was explained by the 4,3 addition of isoprene to the Mg–C_4 carbon bond of **1** and that of the propagation by the 4,3 addition of isoprene to the Mg–C_3 carbon bond. To understand the unique catalytic behavior of the magnesium–isoprene adducts, the initial stages in the polymerization of isoprene catalyzed by Grignard reagents and dialkyl- and dialkenylmagnesium compounds were also investigated.

The initial stages in the n-butyllithium[1–14] or π-allylmetal[15–19] catalyzed oligomerization of conjugated dienes have been extensively studied to clarify the structure of propagating chain ends,[2–8,17–19] association of the "living" oligomer,[9–11] and the effect of ligands on the microstructure of the polymer.[12–14] In contrast to these detailed studies concerning the 1,4 polymer, the corresponding study which deals with the 3,4 polymer has not been undertaken much,[20–22] because of the lack of suitable catalyst systems.

Recently, Ramsden[23] and Akutagawa[24] found that magnesium activated with alkyl halides and/or metal halides can react with various kinds of conjugated dienes to give unusual "magnesium–diene compounds". A new terpenoid synthesis using these systems has recently been reported.[25–29] The remarkably high reactivity of the activated magnesium and the quantitative yield of the linear diene dimers led us to attempt the oligomerization of dienes using this "enediylmetal"[27] system. In a previous paper,[30] we reported the stepwise formation of magnesium–butadiene 1:1, 1:2, 1:3, and 1:4 adducts. Higher oligomers having more than five butadiene units could not be obtained in this case, as the propagating chain ends isomerized to inactive chain ends by ring closure. By contrast, isoprene provided linear 3,4-oligomers in a stepwise manner with this enediylmetal catalyst system. This paper describes the structures and association behavior of the magnesium–isoprene 1:1 (**1**), 1:2 (**2**), 1:3 (**3**), and 1:4 (**4**) adducts which were formed in a stepwise manner in the initial stages in the polymerization and the succeeding process for the formation of 3,4-polyisoprene.

Results and Discussion

Isolation of the Magnesium–Isoprene 1:1, 1:2, and 1:3 Adducts. Isoprene is known to react with magnesium activated with minute quantities of iodine, alkyl halides,[23] and/or metal halides[24] to give the magnesium–isoprene 1:2 adduct. We found that the activated magnesium also functions as a catalyst for the oligomerization of isoprene and the chain growth of the oligomer is dependent on the initial g-atom/mol ratio of magnesium to isoprene. The reaction proceeded by the addition of organic halides to the mixture of magnesium and isoprene only at temperatures higher than 60 °C (method 1) but the resulting magnesium–isoprene adducts were always a mixture; i.e., the reaction of 0.1 molar equiv of isoprene with magnesium at 60 °C gave a mixture of $(\mathrm{MgC_5H_8})_n$ **1** and $(\mathrm{MgC_{10}H_{16}})_n$ **2** in 1:5 ratio. The 1:2 reaction of magnesium with isoprene gave **1**, **2** and $(\mathrm{MgC_{15}H_{24}})_n$ **3** in 1:6:3 ratio. The

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Table I
Characterization of Magnesium–Isoprene Adducts

Compd	% Mg (calcd)[a]	Mol wt (calcd)[b]
$(MgC_5H_8{\cdot}2THF)_n$ (1)	10.3 (10.3)	1195^c (236)
$(MgC_{10}H_{16}{\cdot}2THF)_n$ (2)	7.9 (8.0)	915^c (304) 1205^d
$(MgC_{15}H_{24}{\cdot}2THF)_n$ (3)	6.5 (6.5)	562^c (372) 739^d
$(MgC_{20}H_{32}{\cdot}2THF)_n$ (4)	5.4 (5.5)	450^c (440) 480^d

[a] Determined by the 8-oxyquinolinate method. [b] Calculated as $n = 1$. [c] Determined ebullioscopically in THF. [d] Determined cryoscopically in benzene.

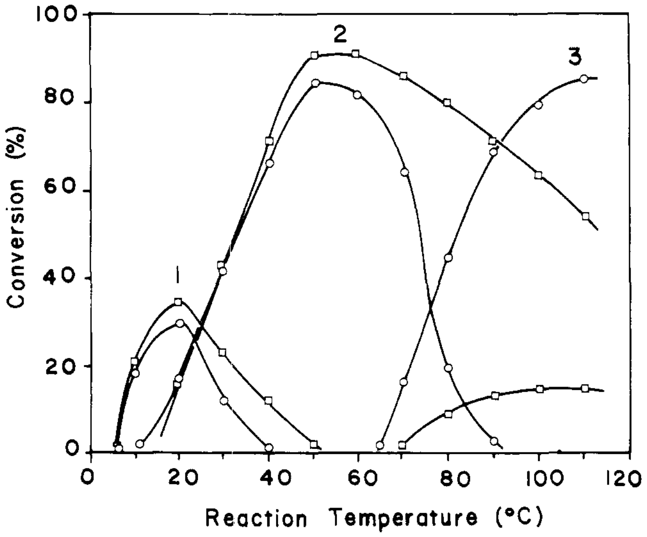


Figure 1. Products distribution vs. reaction temperature in the reaction of magnesium with isoprene in 1:2 (□) and 1:3 (○) ratio. Reaction time, 40 h.

above method was, therefore, unsuitable for the isolation of pure adducts. In our survey for new methods for activation of magnesium turnings, we found that magnesium turnings which were once reacted partially with 0.01 mol of methyl iodide (or iodine) and 0.1–0.2 mol of isoprene at 70 °C, recovered from the solution, and then washed with tetrahydrofuran (THF) had remarkably high reactivity. Magnesium turnings thus obtained reacted with freshly introduced isoprene (0.1–0.5 mol) at temperatures as low as 10–12 °C to give only 1 without further addition of a catalyst (method 2). The isolation of 1 was thus accomplished using method 2. Temperature–conversion curves for the reaction of magnesium (activated by method 2) with isoprene in 1:2 and 1:3 ratios are given in Figure 1. With reference to this curve, the adduct 2 was isolated by the 1:2 reaction at 55–60 °C and 3 by the 1:3 reaction at 95 °C. The adduct 2 could be prepared also by the reaction of an equimolar amount of isoprene with 1 at 55 °C and 3 by the equimolar reaction of isoprene with 2 or the reaction of 2 mol of isoprene with 1 at 90–95 °C. Strict control of the reaction temperature and use of preactivated magnesium are indispensable for the isolation of pure magnesium–isoprene adducts.

The Structure of the Magnesium–Isoprene Compounds in Solution. Characterizations of a series of magnesium–isoprene adducts are given in Table I. Deuterolysis of 1, 2, 3, and 4 gave dideuterated compounds, $C_5H_8D_2$, $C_{10}H_{16}D_2$, $C_{15}H_{24}D_2$, and $C_{20}H_{32}D_2$, respectively, as evidenced by mass spectroscopy, besides the 2 mol of THF which had been coordinated to the magnesium atom. Thus, isoprene moieties in the adducts bind to magnesium atom(s) bifunctionally. The molecular weight of 1 determined ebullioscopically in THF corresponded to the pentamer of $MgC_5H_8{\cdot}2THF$ while that of 2 corresponded to the trimer of $MgC_{10}H_{16}{\cdot}2THF$ and 3 to the intermediate value of monomeric and dimeric $MgC_{15}H_{24}{\cdot}2THF$. Compound 4 and its higher homologues had monomeric structures. In benzene, 2 had tetrameric, 3 had dimeric, and 4 had monomeric structures as determined by the cryoscopic method. The solubility of 1 in benzene was not enough to permit the measurement. The values mentioned above were independent on the concentration of the solution and the result sharply contrasts to the usual behavior of Grignard reagents[31] or dialkylmagnesium compounds[32] which have monomeric structures in THF. Therefore, their high molecular weight should be ascribed to their polymeric structures rather than to their associated or aggregated structures.[30]

Compound 1 thus isolated gave 3-methyl-1-butene (6%), 2-methyl-1-butene (33%), and 2-methyl-2-butene (61%) upon hydrolysis. Compound 2 gave 2,7-dimethyl-1,7-octadiene (35%), 2,7-dimethyl-1,6-octadiene (46%), and 2,7-dimethyl-2,6-octadiene (19%). Compound 3 gave mainly 2,9-dimethyl-5-isopropenyl-1,9-decadiene (85%) and 2,9-dimethyl-5-isopropenyl-1,8-decadiene (9%). The above relations can be explained by Scheme I. Similar equilibriums are pro-

Scheme I

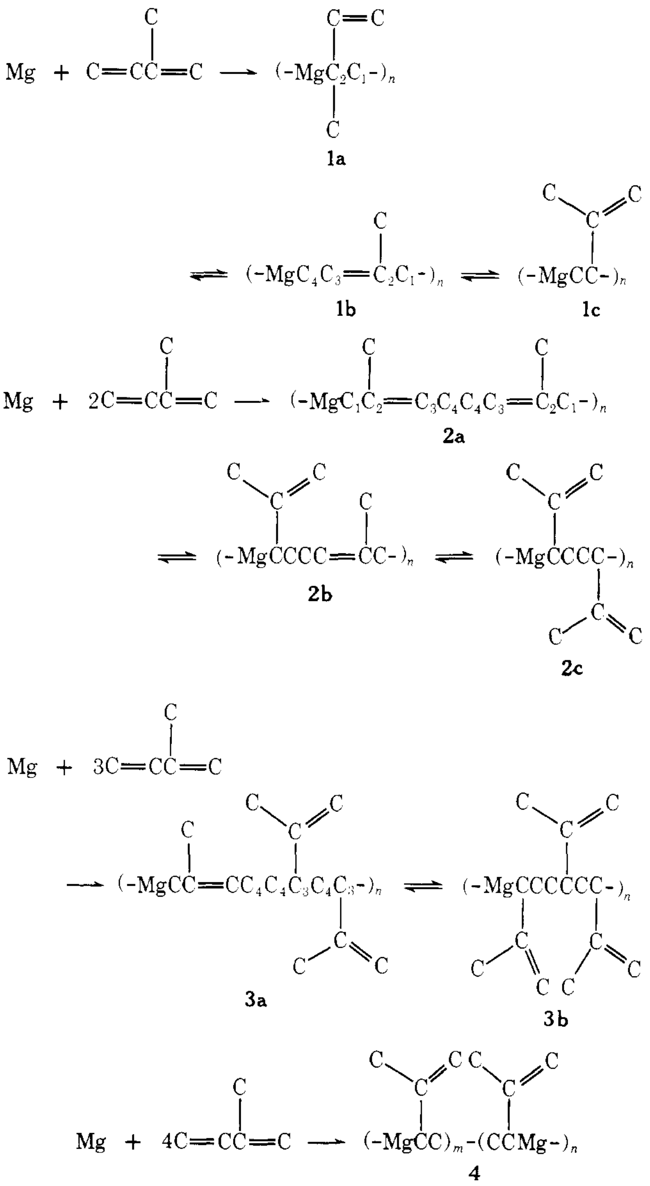


Table II
Distribution (%) of Protolysis Products of 1 and 2[a]

Protolysis reagent	$(MgC_5H_8)_n$ system			$(MgC_{10}H_{16})_n$ system		
	MB-1	MB-2	MB-3	DO-1	DO-2	DO-3
tert-Butyl alcohol	43	43	14	85	11	4
Isopropyl alcohol	35	38	27	75	20	5
H_2O	6	33	61	35	46	19
Piperidine	3	20	77	15	25	60
Pyrrolidine	1	11	88	10	21	69
Me_3NO[b]	0	4	96	8	20	72

[a] MB-1, 3-methyl-1-butene; MB-2, 2-methyl-1-butene; MB-3, 2-methyl-2-butene; DO-1, 2,7-dimethyl-1,7-octadiene; DO-2, 2,7-dimethyl-1,6-octadiene; DO-3, 2,7-dimethyl-2,6-octadiene. [b] Trimethylamine oxide complex was hydrolyzed.

posed for crotylmagnesium compounds by Glutzner.[33] Protolysis of **1**, **2**, and **3** with both acidic and basic reagents provided more exact information concerning the equilibriums shown in Scheme I. Protolysis of **1** and **2** with *tert*-butyl alcohol resulted in the predominant formation of 3-methyl-1-butene and 1,7-dimethyl-1,7-octadiene, respectively, whereas protolysis with bases brought about an increase of 2-methyl-2-butene and 1,7-dimethyl-2,6-octadiene as shown in Table II. In the case of **3**, both acidic and basic reagents gave identical results, i.e., 2,9-dimethyl-5-isopropenyl-1,9-decadiene derived from **3b** was the main product in both cases.

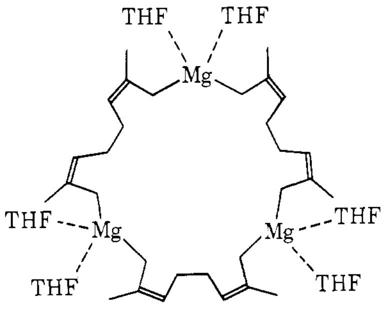
The above results are concordant with the general rule[34,35] that the coordination of strong base causes an increase in ionic character of the metal–carbon bond resulting in the cleavage of the linkage between metal and α-carbon (to give cis isomer) in preference to the cleavage of metal and γ-carbon bond upon hydrolysis. As reported previously,[30] the coordination of *N*-methylpyrrolidine or trimethylamine oxide to magnesium–butadiene 1:1 and 1:2 adducts resulted in the predominant production of *cis*-2-butene and *cis,cis*-2,6-octadiene, respectively, upon hydrolysis following the "cis rule". With a similar concept, the result of base cleavage of **1** can be explained by the cleavage of **1b** and that of acid cleavage by **1a** and **1c**. A similar explanation is also possible for **2**. In the cases of **3** and **4**, the distribution of hydrolysis products was not effected by the nature of the cleaving reagent and their Mg–γ-carbon bonds were cleaved preferentially. The large difference between **2** and **3** observed in hydrolysis, irrespective of their chemical similarity, would be ascribed to the inductive effect of the central C_5H_8 moiety present in the carbon chain of **3** or the weak interaction of its C=C group to magnesium atom(s) as was shown in $Al[(CH_2)_2CH{=}CH_2]_3$.[36] The adducts **7** and **8** (described later) also preferred the Mg–γ-carbon bond, contrary to **5** and **6**. Thus the Mg–α-carbon bond which is generally observed in allylic magnesium compounds can easily convert to the Mg–γ-carbon bond by a slight change of organic substituents. The energy barrier for interconversion between **2a** and **2c** or between **3a** and **3b** is, therefore, considered to be very small.

Nuclear Magnetic Resonance Studies of the Adducts 1–4. To elucidate the structure of the initiating and propagating chain ends, ^{1}H-NMR spectra of **1–4** were taken in THF-d_8 (Table III). The chemical shifts and the mode of splitting of the signals in the spectrum of **1** clearly showed that it assumed the structure **1b** among the three possible structures. No separate spectral resonances attributable to the species **1a**, **1c**, or other organic groups were detected. The structure of **2** was concluded to be **2a** (4,1 chain end) and the signals derived from **2b** or **2c** (4,3 chain end) were not detected in this case also. Di-3-methyl-2-butenylmagnesium **5** and di-2-methyl-2-butenylmagnesium **6** should be useful as model compounds for **1** and **2**, respectively, to reveal the relative magnitude of the electron density on their Mg–C carbon atoms. The CH_2 signals of **1** (Mg–C_4 bond) at δ 0.39 ppm appeared at 0.17 ppm higher field than those of **5** and the other CH_2 signals of **1** (Mg–C_1 bond) at δ 0.45 ppm appeared at 0.3 ppm higher field than those of **6**. The chemical shift difference of CH_2 protons between **2** and **6** was 0.06 ppm. As the chemical shift difference of methyl groups between $(CH_3)_2C{=}CHCH_3$ and $(CH_3)_2C{=}CHCH_2CH_2CH{=}C(CH_3)_2$ is 0.02 ppm and that between $(CH_3)_2C{=}C$ and $CH_3CH{=}C$ groups is within 0.08 ppm, we can conclude from the chemical shift differences and the values of chemical shift that the negative charge density on the Mg–C carbon atoms increased in the following order.

$$\text{Mg–C}_4 \text{ of } \mathbf{1} \geq \text{Mg–C}_1 \text{ of } \mathbf{1} > \text{Mg–C}_4 \text{ of } \mathbf{2} \simeq \text{Mg–C of } \mathbf{5} \text{ and } \mathbf{6}$$

^{1}H-NMR spectrum of **3** showed that it was composed of a mixture of **3a** (20%) and **3b** (80%) in good agreement with the protolysis data. In other words, the ratio of the 4,1 to 4,3 chain ends was 1:14. The corresponding ratio observed for **4** was 1:25. Thus, the 4,1 chain end decreased with an increase in the chain length and finally disappeared in the magnesium–isoprene 1:10 adduct. In the ^{13}C-NMR spectra, as shown in Table III, a similar correspondence in chemical shifts of **1** to **5** and **2** to **6** was observed, but significant differences in chemical shift between the signals of **1** and **5** or between the signals of **2** and **6** were not observed. In both ^{1}H- and ^{13}C-NMR spectra of **1**, **2**, and **5**, any peak splittings derived from the difference of cis and trans configurations were not detected even at low temperatures from 0 to −80 °C.

As mentioned above, the adducts **1–4** were considered to have a polymeric structure. However, resonances attributable to the polymer chain ends were not detected in all of the spectra. The possibility of the presence of a halide group in the polymer chain ends was ruled out by the stoichiometry and no iodide was detected from **1–4** by the silver nitrate test. No organic materials attributable to the polymer ends were detected in the GC analysis either. Therefore, we can reasonably conclude that **1–4** have a macrocyclic structure. The molecular structure of 12-membered ring organomagnesium compounds containing two Mg atoms on the ring was recently reported by Bickelhaupt.[37] Although data on the molecular weight distribution of the magnesium–isoprene adducts are unfortunately lacking, we can estimate the average ring sizes from their molecular weights in THF. Compound **1** was considered to have on average a 25-membered ring structure containing five magnesium atoms on the ring and **2** to have a 27-membered ring structure containing three Mg atoms. The trimer model of **2** may be illustrated as follows.



2

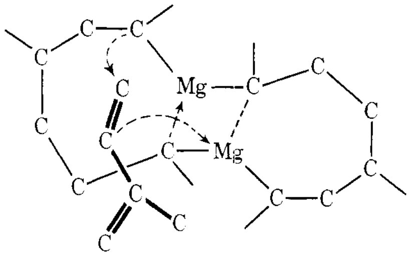
Similar macrocyclic structures having only one magnesium atom on the ring are considered for **4** and its higher homologues. The decrease in number of magnesium atoms on the ring in order of **1** > **2** > **3** > **4** can be explained by considering the intramolecular chain interaction with Mg–C–Mg bridging derived from the electron-deficient bonding and the succeeding migration reaction. For example, the process for the

Table III
Nuclear Magnetic Resonance Chemical Shifts of Adducts 1 and 2 and Model Compounds 5 and 6

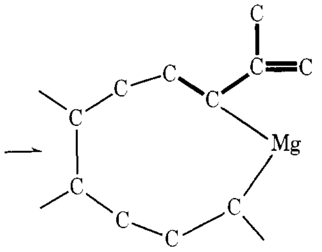
	^{1}H-NMR chemical shift (δ, ppm)[a]				^{13}C-NMR chemical shift (δ, ppm)[b,c]				
	Mg–CH_2	CH_3	CH	CH_2	C_1	C_2	C_3	C_4	C_5
1	0.39 d 0.45 s	1.67 s	4.83 t		16.5	114.7	128.2	21.3	28.9
2	0.69 s	1.67 s	4.21 t	1.99 m	21.6	107.3	145.4	31.4	28.1
5	0.56 d	1.58 s	5.66 t		16.2	135.8	109.9	27.0	
6	0.75 s	1.60 s	4.23 q		20.8	109.0	146.8	27.6	26.0

[a] Data were collected at 100.0 MHz at 35 °C in THF-d_8 and were calibrated using the upfield THF peak assumed to be 1.85 ppm downfield from external Me_4Si. [b] Peak assignments were made in part from an off-resonance decoupled spectrum and data were collected at 25.2 MHz in THF-d_8 at 35 °C using Me_4Si as the external standard. [c] Carbon numbers of 1 and 2 are shown in the scheme and of 5 and 6 are given in formulas **5a** and **6a**.

rink shrinkage of 3 resulting in the formation of 4 can be depicted as follows (dimer model of 3 is illustrated and prenyl groups are omitted).

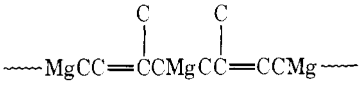


3b



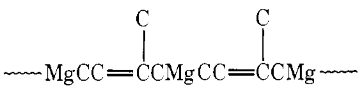
4

For the structure of **1**, three types of bondings, head to head (**1b-I**), head to tail (**1b-II**), and tail to tail (**1b-III**), are possible regarding the adjacent two isoprene moieties. Thermal decomposition of **1** gave information about this. When adduct **1** was heated to 80 °C in THF for 15–120 min, one fifth of magnesium contained in **1** was precipitated accompanying the formation of the 4,4-isoprene dimer unit ($-MgC_{10}H_{16}-$). The molar ratio of the $MgC_{10}H_{16}$ to MgC_5H_8 unit observed in ^{1}H-NMR was 1:3. This result shows that adduct **1** has head-to-head, head-to-tail, and tail-to-tail bondings in 1:3:1 ratio and the 4,4 dimer unit was formed from the tail-to-tail bond.



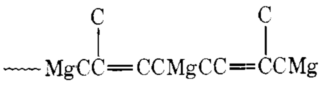
$$—MgCC{=}\overset{C}{C}CMgC\overset{C}{C}{=}CCMg—$$

head to head
Ib-I



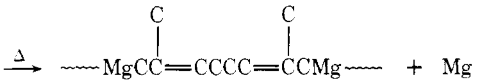
$$—MgCC{=}\overset{C}{C}CMgCC{=}\overset{C}{C}CMg—$$

head to tail
Ib-II



$$—MgC\overset{C}{C}{=}CCMgCC{=}\overset{C}{C}CMg$$

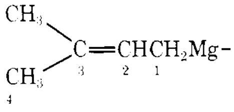
tail to tail
Ib-III



$$\xrightarrow{\Delta} —MgC\overset{C}{C}{=}CCCC{=}\overset{C}{C}CMg— + Mg$$

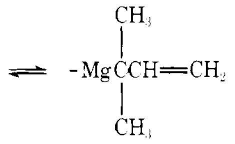
This type of decomposition will however be independent of the propagation of **1** to **2**, because the decomposition did not occur at 80 °C when free isoprene was present and **1** could form **2** at 50–60 °C, at which temperature no decomposition occurred. By contrast, only head-to-head bonding surrounding the magnesium atom is considered for the structure of **2** and no decomposition was observed by heating it to 120 °C.

The Process for the Formation of the Oligomer. Among the C_1–C_4 carbons of compound **1**, the C_4 carbon can be considered to be the most reactive for the insertion of isoprene, as the C_4 carbon of **1** entered into combination selectively with the C_4 carbon of isoprene to form **2**. Two routes are possible for this combination. To elucidate whether **2** is formed via **1b** or **1c**, model examinations were done using di-3-methylbutenylmagnesium **5** and di-2-methylbutenylmagnesium **6**. The reaction of equimoles of **5** with isoprene proceeded via **5b** to give 2,5,5-trimethyl-1,6-heptadiene (95%) and 2,5,5-trimethyl-2,6-heptadiene (5%) upon hydrolysis, while **5** had **5a** structure in solution (see Table III).



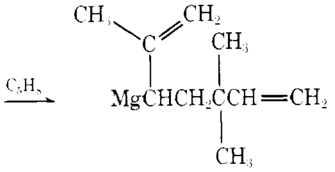
$$(CH_3)_2C{=}CHCH_2Mg-$$

5a



$$\rightleftharpoons -MgC(CH_3)_2CH{=}CH_2$$

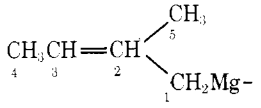
5b



$$\xrightarrow{C_5H_8} MgCH(C(CH_3){=}CH_2)CH_2C(CH_3)_2CH{=}CH_2$$

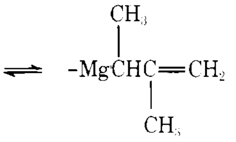
7

Similarly, **6** reacted with isoprene via **6b** to give 2,3,6-trimethyl-1,6-heptadiene (97%).



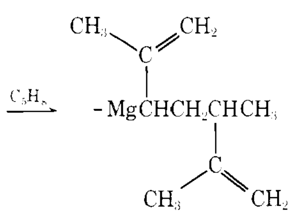
$$CH_3CH{=}C(CH_3)CH_2Mg-$$

6a



$$\rightleftharpoons -MgCH(CH_3)C(CH_3){=}CH_2$$

6b



$$\xrightarrow{C_5H_8} -MgCH(C(CH_3){=}CH_2)CH_2CH(CH_3)C(CH_3){=}CH_2$$

8

Thus, both **5** and **6** having **5a** and **6a** structures in solution converted to **5b** and **6b** by a rapid 1,3 shift, which cannot be

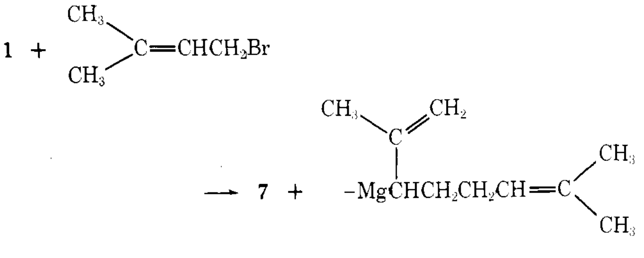
Table IV
The 1:1 and 1:2 Reactions of Organomagnesium Compounds with Isoprene at Various Temperatures

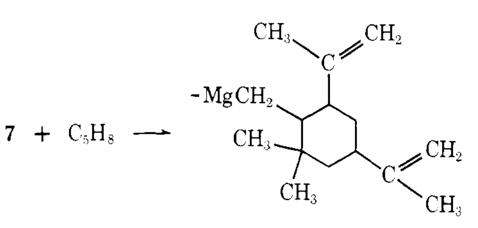
	Yield (%) of 1:1 adduct[a] at temp (°C) =				Yield (%) of 1:2 adduct[b] at temp (°C) =			
	40	60	80	100	40	60	80	100
$(CH_3)_2Mg$	0	0	1	7	0	0	0	2
$(C_2H_5)_2Mg$	0	0	6	17	0	0	0	4
5	0	5	18	81	0	0	9	14
6	0	16	40	88	0	0	11	17
1	10	43	98	99	0	0	24	40

[a] Hydrolysis products were analyzed by GC after the 1:1 mixture was allowed to react for 40 h. [b] Data did not include the yield of the 1:1 adduct formed simultaneously with the 1:2 adduct.

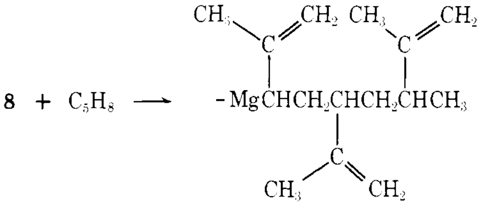
detected on the NMR time scale, when isoprene attacked the compounds. The high reactivity of the Mg–C_4 carbon bond of **1** and the 1,3 shift of **1b** to **1c** was also confirmed by the reaction of 3-methyl-2-butenylbromide with **1**. The prenyl group attacked preferentially the Mg–C_4 carbon bond to form 2,5,5-trimethyl-1,6-heptadiene (45%) and 2,7-dimethyl-1,6-octadiene (38%) upon hydrolysis. These results strongly suggest that the most probable process for the formation of **2** from **1** is via **1c**, not **1b**. Similarly, the formation of **3** can be explained by the 4,3 addition of isoprene to **2c**. That is to say, all the processes, 1 → 2 → 3 → 4 → higher homologues, can be interpreted by the repeating 4,3 addition of isoprene to the Mg–carbon bond in the chain ends. In the initiation step, isoprene inserted to the Mg–C_4 carbon bond of **1**, while in the succeeding propagation step it inserted to the Mg–C_3 carbon bond as the resulting adducts **2**, **3**, **4**, and their higher homologues cannot form the Mg–C_4 bond. Thus, the formation of 3,4-polyisoprene is interpreted by the repeating 4,3 addition of isoprene to the Mg–C_3 chain end.

The Catalytic Activity of the Other Organomagnesium Compounds. Organomagnesium compounds are generally known to be inactive as catalysts for the polymerization of isoprene, while the adducts **1** and **2** have high activities. To understand this difference in reactivity, 1:1 and 1:2 reactions of various kinds of organomagnesium compounds with isoprene were investigated at various temperatures. Dimethyl-, diethyl-, and di-*n*-butylmagnesium had little catalytic activity and Grignard reagents such as methylmagnesium iodide and ethylmagnesium bromide had practically no reactivity toward isoprene even at 80 °C. In contrast, allylic type organomagnesium compounds had high reactivity. Compounds **5** and **6** as well as **1** reacted readily as shown in Table IV. Their high reactivities are attributable to their dynamic structures and to the strong ionic character caused by the inductive effect of the two methyl substituents on the allyl group. The electron is delocalized on the allyl group and, hence, the metal–carbon bond is considered to become more labile than that of alkylmagnesium compounds. The 1:1 reaction of **5** with isoprene was similar to that of **6**. The 1:2 reaction of **5** with isoprene, however, differed from the corresponding reaction of **6**. The former gave a cyclic adduct while the latter gave a linear 1:2 adduct. The ring closure can be explained by the transfer of the magnesium atom to the vinyl end of **7**, as was reported in the 1:2 reaction of crotylmagnesium bromide with isoprene[38,39]





or in the 1:3 reaction of magnesium with butadiene.[30] The ring closure occurred in competition with the formation of a linear oligomer and the relative ratio of cyclic to linear adducts was dependent on the amount of isoprene present in the system. When 2 mol of isoprene was reacted with **5** at 100 °C, the ratio of the cyclic to the linear compound was 95:5, while the ratio reversed to 1:30 by the addition of excess (100 mol) of isoprene to **5**. The cyclic compound **7** obtained from the 1:2 reaction of **5** with isoprene at 100 °C for 5 days had practically no catalytic activity for the oligomerization of isoprene. Thus, the formation of linear adducts having vinyl ends caused ring closure of the chain ends and the successive insertion of the monomer was suppressed by the ring formation. In contrast, magnesium atoms hardly migrate to the propenyl end and, therefore, compound **6** afforded the linear oligomer via **8** without the



accompanying ring formation. In conclusion, the remarkable high reactivity of **1** and **2** can be explained by their dynamic structures, high electron densities on the Mg–C carbon atoms derived from the two adjacent magnesium atoms, and also the formation of propenyl chain ends which did not cause the pseudotermination by ring closure.

Characterization of the Oligomer Obtained with 1 and 2. The oligomerization of isoprene with **1** and **2** was carried out at 60 °C for 40 h. The degree of oligomerization paralleled the initial molar ratio of isoprene to **1** until the ratio became 15. Addition of 100 mol of isoprene to **1** or **2** resulted in the formation of an oligomer having ca. 126 units of isoprene and the addition of 200 mol of isoprene gave an oligomer having ca. 285 units of isoprene. These data followed the calculated curve obtained from both their yields and molecular weights. Consequently, we can conclude that the catalytic efficiency of **1** and **2** is fairly large. In practice, the dispersity indexes of the polymer, M_w/M_n, determined with gel permeation chromatography were close to that of monopersed polymers (Table V).

The polyisoprene obtained with **1** or **2** consists of 90% of 3,4 and 10% of 1,2 and 1,4 units, based on an analysis of its NMR spectrum.[40] The rate of polymerization could be accelerated by the addition of hexamethylphosphorictriamide (HMPA) or by using it as solvent. However, the content of 3,4 units decreased and 1,2 units increased remarkably. The polymerization of isoprene in HMPA at 30 °C for 2 h gave a polymer consisting of the 3,4 unit in 60% and the 1,2 unit in 38%. Thus, the addition of a strong donor to **1** or **2** caused an increase in the ionic character of the Mg–carbon bond[2,21,41] and an acceleration of the rate of polymerization but the stereoregularilty of the resulting polymer decreased. The details of the high polymer will be published elsewhere.

Experimental Section

General. All the operations were performed under argon. Solvents were purified as described previously.[30] Gas chromatographic analysis and separation of the reaction products were made by a Hitachi Model K53 gas chromatograph using a capillary column (HB-2000) and a

Table V
Characterization of the Oligomers Obtained by the Reaction of Isoprene with 1 in Various Ratios

Isoprene added to 1, mol/mol	M_n (M_n calcd)	M_w/M_n
5	345 (340)	1.01
10	693 (680)	1.03
50	3600 (3400)	1.09
100	7900 (6800)	1.13
200	17200 (13600)	1.15
400	37200 (27200)	1.19

Varian-Aerograph Model 700 gas chromatograph. Gel-permeation chromatographic analysis was carried out with a Shimazu Model 830 liquid chromatograph. ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian XL-100-15 spectrometer with a Digilab Model FTS-NTS-NMR 3 fourier transform accessory. The mass spectra were recorded on a Hitachi RMU-7HR spectrometer.

Preparation of Magnesium–Isoprene Adduct 1. To 6.08 g (0.25 g-atom) of magnesium turnings in 80 mL of THF was added 0.32 g (2.5 mg-atom) of iodine and then 2.5 mL (0.025 mol) of isoprene dried over calcium hydride. After the mixture was shaken for 24 h at 70 °C in a temperature-controlled water bath equipped with a vibrator, the resulting yellow green solution was removed using a syringe (method 1) and the residual magnesium was washed with three 50-mL portions of THF. To the magnesium thus activated was added again a mixture of 5.0 mL (0.05 mol) of isoprene and 100 mL of THF and the reaction was carried out at 10–12 °C for 80 h (method 2). The resulting solution was evaporated to dryness, giving 1 as a powdery substance in 85% yield (98% in purity). Deuterolysis of 1 in toluene gave a mixture of 3,4-dideuterio-3-methyl-1-butene, 3,4-dideuterio-2-methyl-1-butene, and 1,4-dideuterio-2-methyl-2-butene, besides the 2 mol of THF coordinated to the magnesium atoms. The position of deuteriums in those isomers was determined by ^{1}H-NMR spectroscopy. The purities of these isomers were determined to be >97% with mass spectra using corresponding hydrolysis products.

Preparation of Magnesium–Isoprene Adduct 2. To 11.8 g (0.05 mol) of 1 in 100 mL of THF was added 5.0 mL (0.05 mol) of isoprene. The mixture was allowed to react at 55 °C for 48 h and then 30 mL of *n*-hexane was added to the resulting yellow solution to precipitate impurities. The upper layer was evaporated to dryness and the resulting viscous solid was extracted with 100 mL of benzene to remove 1. The extract was evaporated to dryness to give 2 in 70% yield (95% purity). Deuterolysis of 2 in benzene gave the following three isomers and 2 mol of THF. The position of deuteriums in each isomer was determined in reference to hydrolysis products and each isomer was reduced on palladium charcoal. 3,6-Dideuterio-2,7-dimethyl-1,7-octadiene: ^{1}H NMR (CDCl$_3$) δ 1.04 (q, 4 H, CH$_2$), 1.32 (s, 6 H, CH$_3$), 1.64 (t, 2 H, CHD), 4.34 (s, 4 H, CH$_2$=); IR (neat) 1653, 884 cm^{-1}. 1,6-Dideuterio-2,7-dimethyl-1,6-octadiene: ^{1}H NMR (CDCl$_3$) δ 1.62 (s, 8 H, CH$_3$ and CH$_2$D), 1.72 (s, 2 H, CH$_2$), 2.01 (m, 3 H, CH$_2$ and CHD), 4.68 (s, 2 H, CH$_2$=), 5.14 (t, 1 H, CH); IR (neat) 1670, 1652, 883, 827 cm^{-1}. 1,8-Dideuterio-2,7-dimethyl-2,6-octadiene: ^{1}H NMR (CDCl$_3$) δ 1.60, 1.68 (s, 10 H, CH$_3$ and CH$_2$D), 1.97 (t, 4 H, CH$_2$), 5.13 (t, 2 H, CH); IR (neat) 1647, 830 cm^{-1}. The purity of these compounds was confirmed to be 98% from the relative intensities of (M$^+$) peaks of $C_{10}H_{16}D_2$ and $C_{10}H_{18}$.

Preparation of Magnesium–Isoprene Adduct 3. A mixture of 15.2 g (0.05 mol) of 2 and 5.0 mL (0.05 mol) of isoprene in 100 mL of THF was heated to 95 °C for 80 h. Adduct 3 was obtained quantitatively as an oily substance by evaporating the solution (in 94% purity). Hydrolysis of 3 in THF gave 2,9-dimethyl-5-isopropenyl-1,9-decadiene (85%), 2,9-dimethyl-5-isopropenyl-1,8-decadiene (10%), and unidentified products (5%) composed of two isomers which could not be separated by GC. Deuterolysis of 3 afforded the following dideuterated products. 3,10-Dideuterio-2,9-dimethyl-5-isopropenyl-1,8-decadiene: ^{1}H NMR (CDCl$_3$) δ 1.04 (4 H, CH$_2$), 1.67, 1.73 (11 H, CH$_3$ and CH$_2$D), 1.87–2.01 (4 H, CH$_2$ and CH), 4.36 (s, 4 H, CH$_2$=), 5.13 (t, 1 H, CH=); IR (neat) 1648, 886 cm^{-1}. 3,8-Dideuterio-2,9-dimethyl-5-isopropenyl-1,9-decadiene: ^{1}H NMR (CDCl$_3$) δ 1.05 (6 H, CH$_2$), 1.60, 1.67 (9 H, CH$_3$), 1.97–2.15 (3 H, CHDC= and CH), 4.38 (s, 6 H, CH$_2$=); IR(neat) 1648, 886 cm^{-1}; mass spectra, (M$^+$) 198 calcd for $C_{15}H_{24}D_2$ and 204 calcd for hydrogenated compound $C_{15}H_{30}D_2$.

Preparation of Magnesium–Isoprene Adduct 4. To 15.2 g (0.05 mol) of 2 in 100 mL of THF was added 10.0 mL (0.1 mol) of isoprene and then the mixture was heated to 90 °C for 80 h. The resulting solution contained 4 (90%), 3 (7%), and (MgC$_{25}$H$_{40}$)$_n$ (3%) as evidenced by GC. Deuterolysis product of 4 was mainly composed of two isomers (90%) which had four isopropenyl groups in the chain. The exact values of *m* and *n* (where $m + n = 4$) expressed in Scheme I were not determined. Mass spectra of the two isomers, (M$^+$) 276 calcd for $C_{20}H_{32}D_2$.

The Reaction of Model Compounds with Isoprene. Model compounds di-3-methyl-2-butenyl- (5) and di-2-methyl-2-butenylmagnesium (6) were prepared by the known methods and purified by recrystallization in THF–*n*-hexane. A mixture of 3.1 g (0.01 mol) of 5 and 1.0 mL (0.01 mol) of isoprene in 20 mL of THF was allowed to react at 70 °C for 80 h. Quenching of the solution with water resulted in the formation of two isomers of $C_{10}H_{18}$ in 83% yield. 2,5,5-Trimethyl-1,6-heptadiene (95%): ^{1}H NMR (CDCl$_3$) δ 0.99 (6 H, CH$_3$), 1.56 (2 H, CH$_2$), 1.69 (3 H, CH$_3$), 1.94 (2 H, CH$_2$), 4.65 (2 H, CH$_2$=), 4.7–5.0 (2 H, CH$_2$=), 5.78 (1 H, CH=); IR (neat) 1640, 908, 886 cm^{-1}. 2,5,5-Trimethyl-2,6-heptadiene (5%): ^{1}H NMR (CDCl$_3$) δ 0.97 (6 H, CH$_3$), 1.62 (6 H, CH$_3$), 2.02 (2 H, CH$_2$), 4.8–5.0 (2 H, CH$_2$=), 5.05 (1 H, CH), 5.73 (1 H, CH); IR (neat) 1642, 909 cm^{-1}. The 1:2 reaction of 5 with isoprene at 90 °C for 100 h gave a cyclic adduct upon hydrolysis. 1,2,2-Trimethyl-4,6-diisopropenylcyclohexane: ^{1}H NMR (CDCl$_3$) δ 0.89 (3 H, CH$_3$), 0.93 (6 H, CH$_3$), 1.61–1.75 (10 H, CH$_3$C= and CH$_2$), 4.71 (4 H, CH$_2$=); IR (neat) 1642, 887 cm^{-1}. Mass spectra, (M$^+$) 206 calcd for $C_{15}H_{26}$ and 210 calcd for the hydrogenated compound, $C_{15}H_{30}$.

In essentially the same way, the reactions of 6 with isoprene in 1:1 and 1:2 ratio were carried out and the following adducts were obtained selectively. 2,3,6-Trimethyl-1,6-heptadiene: ^{1}H NMR (CDCl$_3$) δ 0.98 (d, 3 H, CH$_3$), 1.60 (2 H, CH$_2$), 1.68 (6 H, CH$_3$C), 2.02 (3 H, CH$_2$C= and CH), 4.68 (4 H, CH$_2$=); IR (neat) 1642, 886 cm^{-1}. 2,3,8-Trimethyl-5-isopropenyl-1,9-nonadiene: ^{1}H NMR (CDCl$_3$) δ 0.97 (3 H, CH$_3$), 1.60 (9 H, CH$_3$C=), 1.65 (4 H, CH$_2$), 2.02 (4 H, CH$_2$C= and CH), 4.68 (6 H, CH$_2$=); IR (neat) 1644, 886 cm^{-1}. Mass spectra, (M$^+$) 206 calcd for $C_{15}H_{26}$.

Characterization of the Oligomer. Isoprene oligomers obtained from the reaction of 2 and isoprene in various ratios at 50 °C were analyzed with GPC using myrcene and squalene as the standard of short-chain oligomers and the polyisoprene purchased from Waters Associates as the standard of long-chain oligomers to make calibration curves.

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A ^{13}C NMR Determination of the Comonomer Sequence Distributions in Propylene–Butene-1 Copolymers

James C. Randall

Phillips Petroleum Company, Research and Development, Bartlesville, Oklahoma 74004.

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ABSTRACT: The copolymer composition and dyad, triad, and tetrad sequence distributions have been determined from ^{13}C-NMR data for a series of predominantly isotactic propylene–butene-1 copolymers. The propylene concentrations ranged from 57 to 77 mol %. Number average sequence lengths were determined from the observed dyad distributions and compared to that calculated assuming Bernoullian statistical behavior. A good Bernoullian fit was obtained for both the number average sequence lengths and the associated dyad, triad, and tetrad comonomer distributions. A complete set of NMR schemical shift assignments is given and compared to those predicted with the Grant and Paul parameters and compositional trends observed among the copolymers. A four unit or tetrad sequence was the longest sequence detected by ^{13}C NMR at 25.2 MHz.

A detailed representation of copolymer molecular structure is available from ^{13}C NMR because unlike connecting comonomer sequences can be detected independently of like connecting sequences. Quite often, this structural information is not limited to just dyads but also includes triad, tetrad, and even pentad connecting sequences.[1–3] Thus, copolymer structure can be determined with considerable detail. The translation of ^{13}C-NMR data to meaningful quantitative terms, however, is not always readily accomplished. The observed spectral information is also related to factors other than the simple comonomer distribution. Configuration and mode of addition can seriously complicate analyses of ^{13}C copolymer spectra.[1] All factors must be considered if the information retrieved is to portray accurately the structure of the copolymer system.[1] Correspondingly, the analyses are less tedious and excellent reference information is provided if copolymers are available where configuration is constant and inversions in the mode of monomer additions have not occurred.[2]

The propylene–butene-1 copolymers examined in this study were prepared under polymerization conditions that led to essentially isotactic, head-to-tail comonomer sequences.[4] Thus, inversion in the mode of monomer addition and multiple configurational arrangements were not a consideration in the ^{13}C-NMR analysis. Any multiplicities in chemical shifts for a particular carbon type could be attributed to differences in the comonomer sequence arrangements and not to configurational differences. Recently, in a study of related propylene–butene-1 copolymers, which were prepared with Zeigler catalysts and were rich in butene-1, Fisch and Dannenburg[5] obtained assignments for isotactic butene-1–butene-1 and butene-1–propylene sequences. These assignments have been extended by the present study because the relative concentrations of the two different monomer units in the series of copolymers examined were more nearly the same. Resonances were observed in the ^{13}C spectra for triad and tetrad comonomeric sequences in addition to the isotactic propylene–propylene dyad not detected in the earlier study.

With a finite set of dyads, that is, propylene–propylene (PP), propylene–butene-1 (PB), and butene-1–butene-1 (BB), the number average sequence lengths for both butene-1 and propylene monomer units can be calculated. This determination of number average sequence length is independent of any possible statistical fit or behavior and, therefore, is a true structural characteristic of these propylene–butene-1 copolymers. It is shown in this study that the comonomer sequence arrangements do, however, closely conform to a Bernoullian statistical model.

Experimental Section

The *propylene–butene-1* copolymers examined in this study were prepared by methods reported previously.[4] The copolymer sequences are essentially isotactic and head to tail. Thus, the only structural variations outside of molecular weight and comonomer ratio occur among the arrangements possible for the butene-1 and propylene units. The ^{13}C spectra obtained were totally consistent with predominantly isotactic, head-to-tail sequences because the observed copolymer chemical shifts corresponded to those given in Table I for predominantly isotactic polypropylene and polybutene-1. Nonstereoregular polypropylene[6] and polybutene-1 (as observed in this laboratory) show extensive splittings, which were not observed in these copolymer spectra, for both the side chain and backbone carbon resonances.

Carbon-13 NMR spectra were obtained at 25.2 MHz from a Varian XL-100-15 spectrometer system equipped with a 16K FT-100 pulsed NMR computer system and a disk accessory. Spin–lattice relaxation times were obtained at 123 °C and a sweep width of 2500 Hz for each of the major lines in the ^{13}C copolymer spectra. The methylene carbons, in each location, consistently gave T_1 values below 1 s. The methine carbon T_1's ranged from 0.8 to 1.2 s while the methyl carbon T_1's were approximately 2 s for the propylene units and 3.5 s for the

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