

THE PREPARATION AND SOME REACTIONS OF ISOPRENE-MAGNESIUM COMPOUND

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Although many reports have been published on the preparation of organomagnesium compounds, it is scarcely known that this kind of compounds was prepared by the direct reaction of hydrocarbon with metallic magnesium (1). Recently, Akutagawa, et al. (2) and Ramsden, et al. (3) have found independently that some conjugated dienes reacted with metallic magnesium on heating in tetrahydrofuran, giving organomagnesium compounds, named "diene-magnesium compounds". As a part of the studies on diene-magnesium compounds, we have investigated on the reaction of isoprene with magnesium to prepare "isoprene-magnesium compound" and on its reactivity to aldehydes and ketones.

When a mixture of isoprene and powdered magnesium in tetrahydrofuran was heated under reflux in the presence of a catalyst, magnesium dissolved gradually and a light or dark gray, viscous solution of organomagnesium compound, named conveniently "isoprene-magnesium compound", was formed. As the effective catalysts on this reaction, a couple of Lewis acid such as metal halides and some kinds of reducing agents such as metal hydrides or Grignard reagents was used. Especially, pairs of ferric, titanium, zinc or copper chlorides and Grignard reagents gave good results both in the yield and in the reproducibility of the reaction. It was also observed that the reaction was unaffected essentially by the nature of Grignard reagents such as kinds of the halogens and the hydrocarbon residues. Some of these results are summarized in Table 1.

Hydrolysis of isoprene-magnesium compound with dilute hydrochloric acid gave a mixture of olefins with C<sub>5</sub>-units; C<sub>5</sub>, C<sub>10</sub>, C<sub>15</sub> and so on. This fact shows that isoprene-magnesium compound may be a complex mixture of the adducts of mag-

nesium and isoprene-monomer, dimer, trimer and so on. The reaction conditions shown in Table 1 were the cases where isoprene-monomer-magnesium compound was formed in a higher yield. In the case that the ratio of Mg/isoprene was over 1.5 the C<sub>5</sub>-olefin fraction was held nearly constant, whereas in the case that the ratio of Mg/isoprene was below 1.5 the C<sub>5</sub>-olefin fraction decreased.

Isoprene-magnesium compound produced under the conditions as described above reacted easily with aliphatic aldehydes and ketones. For an example of these reactions, we wish to describe the reaction with isobutyraldehyde.

The reaction of isoprene-magnesium compound with a molar equivalent amount of isobutyraldehyde was exothermic and gave a mixture of alcohols (I)-(VII). Each product was isolated and purified by means of fractional distillations followed by preparative gaschromatography and/or column chromatography, and their structures were determined by the elemental analyses, the spectral data of the nmr, ir and

Table 1 The Effective Catalysts for the Formation of Isoprene-magnesium Compound (Ip-Mg)<sup>a</sup> and the Compositions of the Hydrolysis Products

Catalysts	Yield of Ip-Mg % <sup>b</sup>	Hydrolysis products of Ip-Mg % <sup>c</sup>		
		C <sub>5</sub> -Olefin	C <sub>10</sub> -Olefin	The others
FeCl <sub>3</sub> + EtMgBr	86	70.4	16.4	13.2
AlCl <sub>3</sub> + EtMgBr	73	67.2	11.8	21.0
ZnCl <sub>2</sub> + EtMgBr	82	62.5	19.3	18.2
CoCl <sub>2</sub> + EtMgBr	70(6 hrs)	48.4	23.8	27.8
NiCl <sub>2</sub> + EtMgBr	50(16 hrs)			
PdCl <sub>2</sub> + EtMgBr	77	56.8	19.2	24.0
TiCl <sub>4</sub> + EtMgBr	86	61.8	19.4	18.8
Cu <sub>2</sub> Cl <sub>2</sub> + EtMgBr	71(7 hrs)	55.9	4.2	39.9
FeCl <sub>3</sub> + LiAlH <sub>4</sub>	57	47.8	21.8	30.4
AlCl <sub>3</sub> + LiAlH <sub>4</sub>	64	56.8	14.3	28.9
ZnCl <sub>2</sub> + LiAlH <sub>4</sub>	64	53.4	20.0	26.6
FeCl <sub>3</sub> + NaBH <sub>4</sub>	48	50.7	6.8	42.5
ZnCl <sub>2</sub> + NaBH <sub>4</sub>	57			

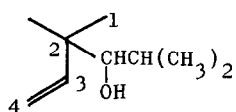
- a Reactions were conducted on using 1.5 mole ratio of Mg/isoprene under reflux for 4 hours. The amount of catalysts used was 5% molar equivalent for Mg.
- b Refers to the yields of Ip-Mg, estimated from the amount of magnesium dissolved (4), based on isoprene used.
- c Refers to the percentage composition of the olefin products.

mass spectroscopy, and some chemical reactions. Details of these results will be published separately.

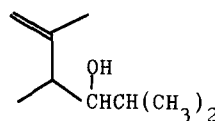
The reaction products of isoprene-magnesium compound with isobutyraldehyde could be classified in the following four kinds of groups (A ~ D):

(A); one to one adducts of isoprene-monomer-magnesium compound and isobutyraldehyde; (I)-(IV).

(B); one to two adducts of isoprene-monomer-magnesium compound and isobutyraldehyde; (V) and its isomers.

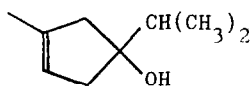
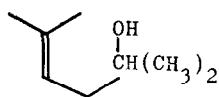


I 4.9%\*

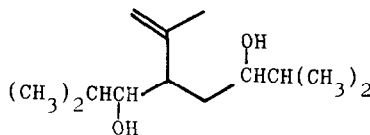


IIa, erythro 4.7%

IIb, threo 4.8%

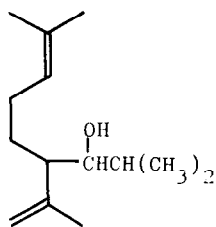


III }  
 IV }  
 0.5%

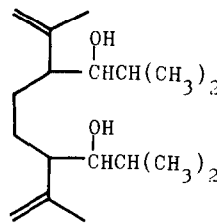


V ( and its isomers)

11.2%



VIa, erythro }  
 VIb, threo } 1.4%



VII, two stereoisomers

&gt; 2%

\* Refers to the yields of the products based on isoprene-magnesium compound produced.

(C); one to one adducts of isoprene-dimer-magnesium compound and isobutyraldehyde; (VI).

(D); one to two adducts of isoprene-dimer-magnesium compound and isobutyraldehyde; (VII).

In the cases of n-propionaldehyde, acetone, diethyl ketone and cyclohexanone, the patterns of the reaction products were closely similar to that in the case of isobutyraldehyde. The yields of the products indicated that aliphatic aldehydes or ketones reacted mainly at the 2- or 3-positions of the isoprene skeleton in the formation of the group (A) products, and at the 3- and 4-positions in the formation of the group (B) products. The formation of the compounds (IV, V, VII) suggests that isoprene-magnesium compound contains bifunctional organomagnesium compounds. Further investigation on isoprene-magnesium compound is now in progress.

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