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STUDIES ON ISOPRENE-MAGNESIUM COMPOUND II.
THE REACTION OF ISOPRENE-MAGNESIUM COMPOUND WITH SOME ESTERS

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As has been reported in a previous paper 1), it has been found that isoprene-magnesium compound, an organomagnesium compound, was obtained by the reaction of isoprene and metallic magnesium and its reaction with aliphatic aldehydes or ketones gave addition products. This paper will describe the reaction of isoprene-magnesium compound with some esters; this gave products which were formed by a reaction mode being different from that in the case with aldehydes or ketones.

Isoprene-magnesium compound, prepared by the method described previously 1), reacted exothermically with aliphatic esters, such as ethyl formate, ethyl acetate, methyl n-butyrate or methyl isobutyrate, giving complex mixtures of many compounds respectively. Each component which was included in a low-boiling fraction of these mixtures was isolated by means of fractional distillations followed by preparative gaschromatographies. The compounds (I~VIII) thus isolated were shown in Chart and their yields were summarized in Table 1. Their structures were determined on the basis of the results of the elementary analyses, the spectral data (nmr, ir and mass), and observation on some chemical reactions. The details of these results will be published in a full paper.

As has been described in the previous paper, the reaction of isoprene-magnesium compound with aliphatic aldehydes or ketones gave such alcohols, monools (1:1 adducts) and diols (2:1 adducts) that were formed by the reaction in which

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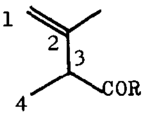
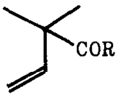


I



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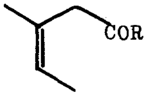

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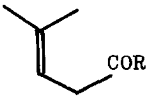

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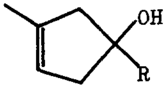

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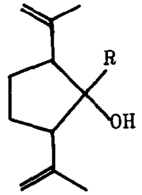
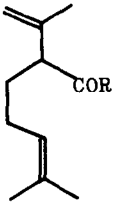
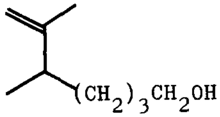


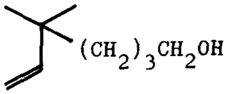
VI, two stereoisomers



VII



VIIIa



VIIIb

Table 1. The Products of the Reaction of Isoprene-magnesium Compound with Aliphatic Esters, RCO_2R' ($R'=CH_3$ or CH_2CH_3). Yield mol %$^{a)}$.

R	I,II	III	IV	V	VI	VII	VIIIa,b
H	—$^{b)}$	> 16.6		trace	—$^{c)}$	—$^{c)}$	
CH_3	trace	6.3	11.2	4.2		22.3$^{d)}$	
$(CH_2)_2CH_3$	1.7	1.7	4.0	16.9	5.0	2.8	7.7$^{e)}$
$CH(CH_3)_2$	1.2	1.2	3.4	28.0	4.4	4.5	6.7$^{e)}$

a) Refers to the yields of the products based on isoprene-magnesium compound, determined by glpc analyses.

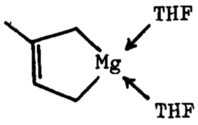
b) The separation of these compounds from the solvent was so difficult that the yield could not be determined.

c) The existence of these compounds could not be confirmed gaschromatographically.

d) A mixture of VI, VII, and VIIIa,b.

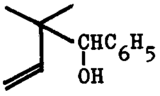
e) The yields varied in accordance with the conditions under which isoprene-magnesium compound was prepared.

the carbonyl compounds reacted with isoprene-monomer-magnesium compound at the 2- or 3- position or at the 3- and 4-positions of the isoprene skeleton, as the major products. On the contrary, the reaction of isoprene-magnesium compound with aliphatic esters scarcely gave products (I and II) which would be expected to be formed by the reaction mode similar to that in the case with aliphatic aldehydes or ketones, but gave carbonyl compounds (III and IV) as the major products. These products must be formed by the reaction in which esters reacted with isoprene-monomer-magnesium compound at the 1- or 4-position. Moreover, it is interesting that this reaction also gave 3-cyclohepten-1-ol derivatives (V) which were formed by a two-steps reaction between a molecule of isoprene-monomer-magnesium compound and a molecule of esters. The formation of V suggests an existence of a divalent isoprene-monomer-magnesium compound, as is represented by Fomula (A). The yields of (V) increased in accordance with the bulkiness of the esters. The compounds (VI) and (VII) were assumed to be formed by the reaction of isoprene-dimer-magnesium compound with esters. Moreover, the compounds (VIIIa) and (VIIIb) were assumed to be formed by the reaction of isoprene-monomer-magnesium compound with tetrahydrofuran used as a solvent. From the findings described above, it was made clear that the reaction mode of isoprene-magnesium compound toward esters was markedly different from that toward aliphatic aldehydes or ketones.

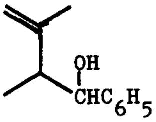


(A)

Benzaldehyde also reacted with isoprene-magnesium compound, giving alcohols (IX, X and XI), together with a small amounts of ketones (XII and XIII). In this case the reaction takes place at the 2- , 3- and 4-positions of isoprene skeleton. The yields of the products indicate that the reaction mode of this reagent toward benzaldehyde is rather similar to that toward esters than that toward aldehydes or ketones. The formation of the ketones, XII and XIII is presumed to be formed by the Oppenauer-type oxidation of the alcohols, IX and X, under these conditions. On the other hand, the reaction of isoprene-magnesium compound with ethyl benzoate resulted in the recovery of the starting material. This suggests that the reac-

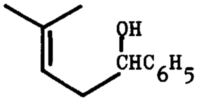


IX



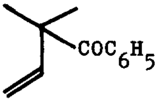
X, erythro and threo

IX + X: 11.2%

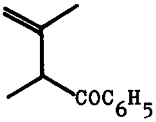


XI

20.1%



XII



XIII

XII + XIII: 0.6%

tivity of isoprene-magnesium compound was lesser than that of the Grignard reagent.

In order to illustrate the difference of the reaction mode between aliphatic aldehydes or ketones and esters, a study on the reaction mechanism is now in progress.

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REFERENCE

1) Meihui Yang, Kazuhiko Yamamoto, Nobumasa Otake, Masayoshi Ando and Kahei Takase Tetrahedron Letters, 1970, 3843.