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ON THE REACTION BETWEEN MAGNESIUM AND ISOPRENE

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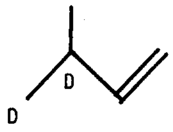
Recently, isoprene-magnesium compounds were prepared by Ramsden[1] and Akutagawa[2], and its reactions with various carbonyl compounds were reported by Takase et al[3]. In our preceding paper[4], the isolation and the reactions toward Lewis acids and bases of the magnesium compounds of butadiene and its dimer were described. We report the difference in catalytic behavior observed between alkyl halide and transition metal halide in the reaction of metallic magnesium with isoprene (IP).

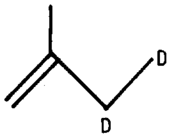
The reaction condition was the same as that in the case of butadiene[4]. The deuterolysis products of the reaction mixture obtained from magnesium and IP (mol ratio, 1:2) were fractionated by recticification into C_5, C_{10} and C_{15} hydrocarbons, and each fraction was further fractionated by preparative glpc. Each component thus obtained was characterized by nmr, ir and mass spectroscopy.

The reaction catalyzed by alkyl halide (1 mol-% of Mg) gave only dideuterio products, of which 5% was pentenes (I-d_2 through III-d_2) and 75% was decadienes (IV-$d_2$through IX-d_2). The structures of the dimers support the structure of IP dimer-Mg compound proposed by Ramsden. The relative amount of isomers depends on the nature of hydrolysis agent (Table 1): the acidic agent favors the terminal double bond and the basic one the inner one, quite similarly to those reported in a preceding paper[4]. No change of skeletal structure was occurred in this process.

The reaction catalyzed by transition metal halide (1 mol-% of Mg) gave the results different from those described above. First, when small amount of $NiBr_2(PPh_3)_2$ was used as catalyst, free pentenes (I, II, III) and free C_{10} hydrocarbons were obtained without hydrolysis in 5% and 10%



I-d_2



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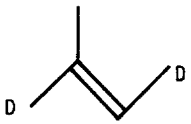

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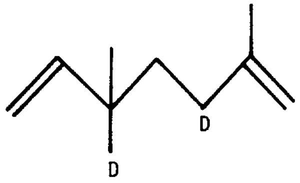

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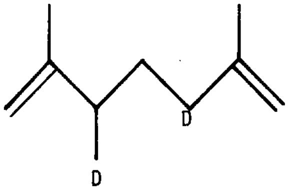

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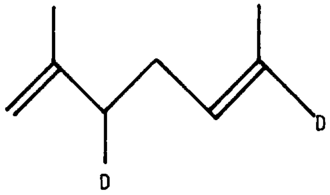

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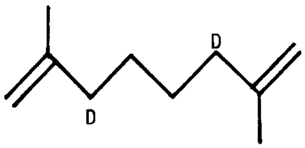

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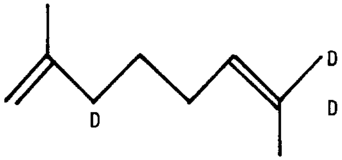

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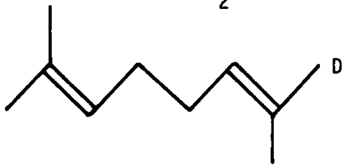
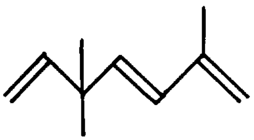


IX-d_2

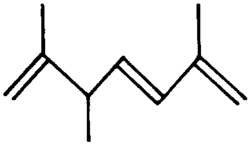
Table 1. Dependence of the relative amount of double bond isomers on the nature of hydrolysis agent. (Hydrolysis temperature, 40°C)

	Monomers			3,4-Dimers		4,4-Dimers		
	I	II	III	V	VI	VII	VIII	IX
$AlCl_3$-H_2O[a]	80	16	4	-	-	-	-	-
t-BuOH	43	41	16	45	55	85	11	4
H_2O	6	33	61	34	66	35	46	19
Pyrrolidine	1	11	88	2	98	10	21	69
Me_3NO-H_2O[a]	0	4	96	3	97	10	21	69

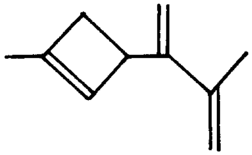
a. Hydrolyzed with water after an equimolar amount of $AlCl_3$ or Me_3NO to reacted magnesium metal was reacted



X



XI



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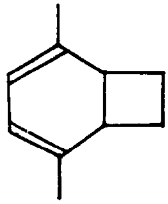
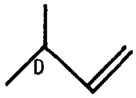


XIII

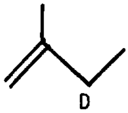
Table 2. Relative amount of the skeletal structure isomers of linear dimers $C_{10}H_{18}$ obtained by hydrolysis with water[a]

Catalyst	2-4 (%)	3-4 (%)	4-4 (%)	1-4 (%)	1-1 (%)
EtBr	5	20	60	12	3
$NiBr_2(PPh_3)_2$	1	9	24	56	10
$PdCl_2(PPh_3)_2$	1	8	40	16	35

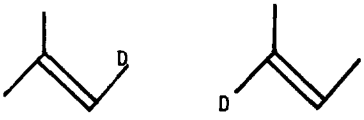
a. The isomers were expressed by the mode of linkage between two IP units.



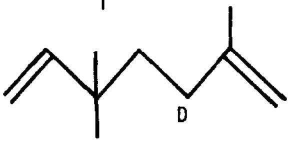
I-d_1



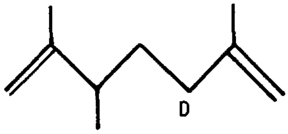
II-d_1



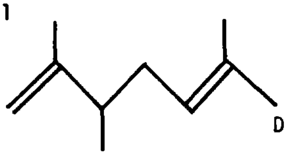
III-d_1



IV-d_1



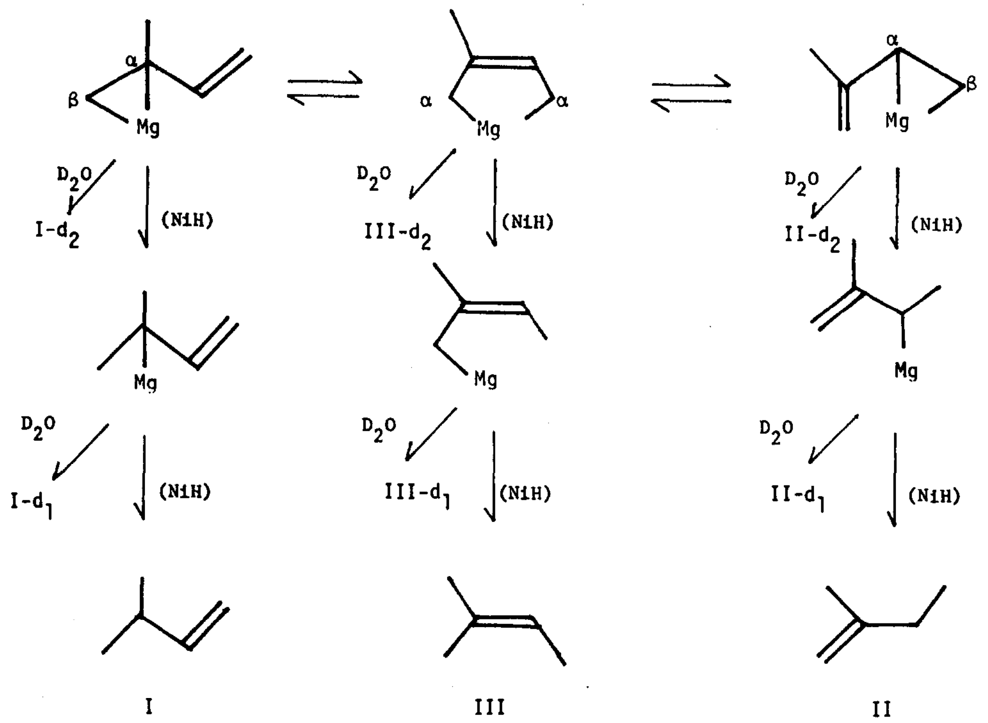
V-d_1



VI-d_1

yield, respectively, based on IP. These C_{10} hydrocarbons are composed of 15% of linear decadienes $C_{10}H_{18}$ (IV, V, VI), 30% of linear decatrienes $C_{10}H_{16}$ (X, XI), 6% of monocyclic decatriene $C_{10}H_{14}$ (XII), 4% of bicyclic decadiene $C_{10}H_{14}$ (XIII) and 45% of monocyclic decadienes $C_{10}H_{16}$ (pinenes, dimethyl-1,5-cyclooctadienes and dimethyl-4-vinylcyclohexenes). Second, the relative amount of skeletal structure isomers of C_{10} hydrocarbons obtained by hydrolysis depended on the nature of catalyst: $NiBr_2(PPh_3)_2$ favored 1,4-dimers and $PdCl_2(PPh_3)_2$ favored 1,1-dimers as shown in Table 2. Third, C_5 hydrocarbon fraction of the deuterolysis product of the $NiBr_2(PPh_3)_2$ catalyzed product obtained in relatively good yield (25%) is composed of only monodeuterio derivatives (I-d_1 through VI-d_1). This result suggests that the magnesium compounds are formed partially accompanied by hydrogen transfer which is presumably catalyzed by the nickel hydride equivalent [NiH] produced by the reduction of $NiBr_2(PPh_3)_2$ by the organomagnesiums. The hydrogen atom(s) proved to originate from IP dimers and trimers, not from the solvent: no deuterium atom was present in the hydrolysis products of the magnesium compounds prepared in THF-d_8 solution, and dehydrogenated IP dimers and trimers were obtained as described above.

It is pertinent to point out that the location(s) of deuterium atom(s) in the mono- and dideuterio C_5 and C_{10} hydrocarbons suggest that the magnesium atom in monohydrogenated magnesium compound links to α-, not β-, carbon atom to the double bond. This fact suggests that the nickel hydride equivalent hydrogenates preferentially one of the two Mg-C bonds to form allyl magnesium compound as illustrated for IP-Mg compounds.



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