

# THE KHARASCH TYPE REACTION OF ALLYLIC HALIDES WITH GRIGNARD REAGENT IN THE PRESENCE OF TRANSITION METAL HALIDES

Y. OHBE\* and T. MATSUDA

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki Higashi-ku, Fukuoka, Japan

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**Abstract**—The reaction of allylic halide with Grignard reagent in the presence of transition metal chloride has been investigated. Three reactions of allylic halide occurred competitively: (i) reduction to olefin, (ii) coupling with Grignard reagent to olefin (cross-coupling) and (iii) coupling with itself to 1,5-diene (homo-coupling). The relative importance of these reactions depends on both the structures of allylic halide and Grignard reagent, as well as on the transition metal salt utilized. The mechanism was discussed in terms of the allylic transition metal intermediate.

## INTRODUCTION

In a previous paper,<sup>1</sup> we examined the catalytic effect of a variety of metallic chlorides on the coupling reaction of alkyl halides in ethereal Grignard reagent solution, which is commonly known as the Kharasch reaction. Although minor variations were found in the catalytic behaviour among the transition metal salts utilized, no marked differences were observed in the nature of the product. Tamura and Kochi<sup>2</sup> investigated the mechanism of the Kharasch reaction extensively and proposed that the reactive intermediate is an alkyl metal species, which is formed from reduced metal and alkyl halide. An extension of this proposition to the reaction between Grignard reagent and an allylic halide in place of the alkyl halide would lead to the formation of an allylic metal intermediate. Under this supposition, it could be anticipated that a possible stabilization of the intermediate which is expected by coordination of a neighbouring double bond to metal,<sup>†</sup> and the use of reactive allylic halide may alter the course of the Kharasch reaction and enhance the difference in the catalytic function of these metal catalysts.

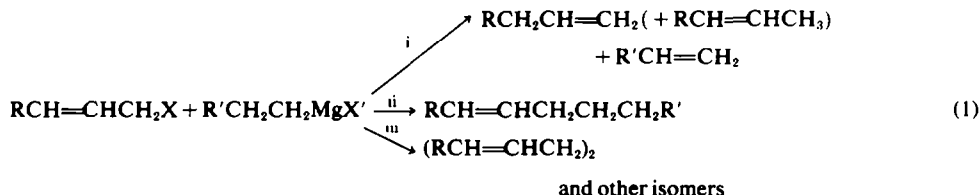
<sup>†</sup> It has been proposed that the iron-catalyzed coupling of 1-alkenyl halides with Grignard reagent differed from that of alkyl halides and coordination of active iron species to double bond might be involved in the former.<sup>3</sup>

In consideration of our previous results,<sup>4</sup> the catalytic reaction of allylic halide with Grignard reagent would be described as in Eq (1); formation of olefin from allylic halide via transfer of hydrogen from Grignard reagent (pathway i), cross-coupling between allylic halide and Grignard reagent (pathway ii) and homo-coupling of allylic halides themselves (pathway iii).

The present work was undertaken to clarify the factors which determine the outcome of these competitive reaction pathways and to obtain an insight into the function of the transition metal catalysis. Crotyl chloride, bromide and iodide were used as well as allyl chloride, while the Grignard reagents were methyl-, ethyl-, and n-propylmagnesium halides. The metallic halides (FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub> and CuCl<sub>2</sub>) were used in variable concentrations.

## RESULTS AND DISCUSSION

*Reaction of crotyl halides with ethylmagnesium bromide.* All reactions in the present paper were carried out in anhydrous ether and by a two-step procedure. Thus the reaction of Grignard reagent with a catalytic amount of metallic salt was carried out under reflux until the gas evolution ceased (reaction A), and then allylic halide was allowed to react with the resultant dark mixture (reaction B).



Reaction of ethylmagnesium bromide (0.1 mol) with crotyl chloride (0.1 mol) in the presence of ferric chloride ( $5 \times 10^{-4}$  mol) gave a mixture of unsaturated hydrocarbons as liquid product in a yield of 58%, which contained three components as shown in Fig 1.

Each peak in Fig 1 was separated by gas chromatography and the constituents afforded the analytical data shown in Table 1. Careful examination of their NMR spectra, as well as other instrumental analysis were consistent with the assignment that the shoulders in the peaks II and III were due to the presence of their *cis* isomers and that the unresolved peak I corresponded to *meso* and *dl* isomers.

Thus, these products are the isomers of  $C_8$  dienes

which were derived formally from coupling of crotyl chloride ( $\gamma$ -methallyl chloride) and/or isomeric  $\alpha$ -methallyl chloride (pathway iii). Table 2 illustrates the effects of halogen in the reaction of crotyl halides in the presence of various metallic salts upon the yield and the composition of gaseous and liquid products in reaction B. In the absence of catalyst, the coupling products were not formed from crotyl chloride, except for a small amount of *trans*-hexene-2. Although the bromide and the iodide afforded the diene products without catalyst, yields of the dienes were much lower than those under the catalytic conditions.

*Reaction with other Grignard reagents.* In Table 3, essential part of the previous results<sup>4</sup> is reproduced to permit a convenient comparison with

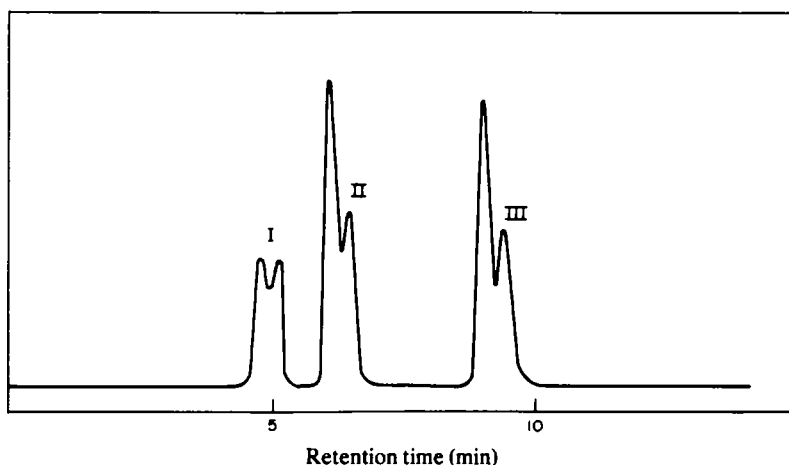


Fig 1. Products obtained from crotyl halide and ethylmagnesium bromide in the presence of Fe(III) chloride

(I) 3,4-Dimethyl-1,5-hexadiene (*dl* and *meso*)

(II) 3-Methyl-1,5-heptadiene (*trans* and *cis*)

(III) 2,6-Octadiene (*trans* and *cis*)

Column: Silicon 703 20%-Celite 545, 3 mm  $\times$  2 m 50°C  $H_2$  60 ml/min

Table 1. Analytical data for the three components in Fig 1

	IR, $cm^{-1}$	NMR, ppm	MS, $m/e$	Structure	
Peak I	1820, 1645	0.93	6H	110	$CH_3-CH-CH=CH_2$
	1425, 995, 910	2.00	2H		$CH_3-\underset{ }{CH}-CH=CH_2$
		4.80	4H		
		5.58	2H		
Peak II	1820, 1675	0.93	3H	110	$CH_3-CH-CH=CH_2$
	995, 965, 910	1.62	3H		$\underset{ }{CH_2}-CH=CH-CH_3$
		2.08	3H		
		4.80	2H		
		5.58	3H		
Peak III	1675, 965	1.62	6H	110	$(CH_3-CH=CH-CH_2-)_2$
		1.95	4H		
		5.30	4H		

Table 2. Products in the reaction of crotyl halides with ethylmagnesium bromide and methylmagnesium iodide<sup>a</sup>

		C <sub>2</sub> H <sub>5</sub> MgBr										CH <sub>3</sub> MgI		
		C <sub>4</sub> H <sub>7</sub> Cl					C <sub>4</sub> H <sub>7</sub> Br					C <sub>4</sub> H <sub>7</sub> I	C <sub>4</sub> H <sub>7</sub> Cl	
		Non	FeCl <sub>3</sub>	CuCl <sub>2</sub>	NiCl <sub>2</sub>	CoCl <sub>2</sub>	Non	FeCl <sub>3</sub>	CuCl <sub>2</sub>	NiCl <sub>2</sub>	CoCl <sub>2</sub>	Non	FeCl <sub>3</sub>	FeCl <sub>3</sub>
B reac. gas <sup>b</sup>	Methane	—	—	—	—	—	—	—	—	—	—	—	—	91
	Ethane	76	42	28	22	30	70	43	43	38	44	60	44	—
	Ethylene	15	50	55	66	62	23	52	51	53	52	40	52	—
	Butane	9	6	15	8	7	7	4	6	7	3	trace	4	—
	Butene	0	2	2	4	3	0	1	trace	2	1	0	trace	8
	Total (l)	0.36	2.39	2.34	2.34	2.36	0.38	2.30	2.21	2.32	2.34	0.38	2.34	2.32
Liq. prod. <sup>c</sup>	<i>trans</i> -Hexene-2	5.9	0	0	0	0	7.1	0	0	0	0	19.0	0.4	—
	I	0	7.2	9.1	7.2	7.2	3.6	12.7	10.9	10.9	9.1	3.6	10.9	9.0
	II	0	25.4	18.2	18.2	23.6	7.2	25.4	25.4	25.4	21.8	12.7	30.9	31.0
	III	0	25.4	21.8	21.8	23.6	1.8	25.4	27.3	25.4	21.8	3.6	30.9	31.0
	Total yields of the dienes	0	58.0	49.1	47.2	54.4	12.6	63.5	63.6	61.7	52.7	19.9	72.7	73.0

<sup>a</sup>Equimolar amount (0.1 mol) of the reagents and  $5 \times 10^{-4}$  mol of each metallic salt were used.<sup>b</sup>Values indicate volume percent of the gaseous products in the B reaction and the total amount in litre.<sup>c</sup>Yields (%) based on 0.1 mol of the halides.

Table 3. Products in the reaction of allyl chloride with n-butylmagnesium bromide<sup>a</sup>

	Catalyst × 10 <sup>-4</sup> mol	FeCl <sub>3</sub>		CuCl <sub>2</sub>		NiCl <sub>2</sub>		CoCl <sub>2</sub>	
		1	5	1	5	0.1	1	0.1	2
B reac. gas <sup>b</sup>	Propylene	62	28	14	11	49	46	51	19
	Butane	14	23	38	31	1	1	1	3
	Butene	24	49	48	58	50	53	48	71
	Total, (l)	1.10	1.94	1.14	3.46	6.36	6.85	7.30	7.85
Liq. prod. <sup>c</sup>	n-Octane	13.1	13.1	20.1	12.7	5.3	7.0	7.9	7.0
	Heptene-1	30.6	48.4	48.4	16.8	2.5	2.5	3.0	0.5
	1.5-Hexadiene	9.7	13.4	13.3	23.1	3.7	2.4	0.6	0.7

<sup>a</sup>Reactions were carried out with 0.2 mol scale.<sup>b,c</sup>Same as in Table 2.

the results in Table 2. It is clear that there are marked differences between allyl chloride and crotyl halides in the nature of the products and the catalytic function of the four catalysts. Thus, crotyl halides are converted almost entirely into C<sub>8</sub> dienes and only small portions are reduced by Grignard reagent to butenes. No meaningful specificity among the catalysts was observed (Table 2). On the other hand, the most of allyl chloride is reduced to propylene [Ni(II) or Co(II)].

In order to understand the different behavior of these two halides, dependence of the product composition on Grignard reagent was examined under several combinations of Grignard reagent and allylic chlorides, and the results in Tables 4 and 5 were obtained. In these combinations the

\*Reaction of crotylmagnesium chloride with ethyl bromide in the presence of ferric chloride was found to give the dienes in the ratio I:II:III = 2:5:2.5.

Grignard reagent was so selected that one could identify the olefins in the product whether they came from Grignard reagent or allylic chloride. It is interesting that in the reaction with methylmagnesium iodide, allyl chloride gave a large amount of 1,5-hexadiene and butene-1, but only a trace of propylene even in the presence of Ni(II) or Co(II) chlorides (Table 5).

*Catalytic and non-catalytic processes.* As shown in Table 2, the reaction of crotyl halides with ethylmagnesium bromide gave a mixture of three dienes of similar composition irrespective of the catalyst utilized. Henne *et al.*<sup>5</sup> reported that the Grignard solution prepared from crotyl chloride ( $\gamma$ -methallyl chloride) or isomeric  $\alpha$ -methallyl chloride afforded a mixture of dienes in the ratio of I:II:III = 2 ~ 3:19:1 after hydrolysis. This seems to be in line with the results obtained in the non-catalytic reactions of crotyl bromide and iodide in Table 2.\* Thus the formation of the dienes under

Table 4. Products in the reaction of crotyl chloride with n-propylmagnesium bromide<sup>a</sup>

	Catalyst × 10 <sup>-4</sup> mol	FeCl <sub>2</sub>		CuCl <sub>2</sub>		NiCl <sub>2</sub>			CoCl <sub>2</sub>		
		5	5	1	2	5	1	2	5		
B reac. gas <sup>b</sup>	Propane	24	32	5	7	5	21	17	22		
	Propylene	55	52	54	55	62	50	54	58		
	Butene-1	17	14	25	24	21	16	16	14		
	Butene-2	4	2	16	14	12	13	13	8		
	Total, (l)	2.87	2.69	2.77	3.07	2.76	3.18	3.30	2.79		
Liq. prod. <sup>c</sup>	n-Hexane	5.0	2.5	0.9	2.3	2.5	0.4	0.5	2.5		
	t-Heptene-2	4.1	3.4	9.0	9.1	5.7	1.0	1.0	3.4		
	I	7.3	11.0	3.6	5.4	1.8	7.2	7.2	7.3		
	II	18.1	23.6	5.4	11.0	5.5	16.3	16.3	18.1		
	III	18.1	21.8	7.2	9.1	5.5	18.0	18.1	18.1		
	Total yields of the dienes	43.5	56.4	16.2	25.5	12.8	41.5	41.6	43.5		

<sup>a,b,c</sup>Same as in Table 2.

Table 5. Products in the reaction of allyl chloride with ethylmagnesium bromide and methylmagnesium iodide

Catalyst × 10 <sup>-4</sup> mol	C <sub>2</sub> H <sub>5</sub> MgBr								CH <sub>3</sub> MgI			
	FeCl <sub>3</sub>		CuCl <sub>2</sub>		NiCl <sub>2</sub>			CoCl <sub>2</sub>		FeCl <sub>3</sub>	NiCl <sub>2</sub>	CoCl <sub>2</sub>
	5	5	1	2	5	1	2	5	5	5	5	
B reac. gas	Methane	—	—	—	—	—	—	—	—	47	1	t
	Ethane	20	27	1	1	1	t	t	1	10	56	21
	Ethylene	46	38	46	52	45	47	49	46	11	—	—
	Propylene	30	13	52	45	53	51	51	54	17	t	t
	n-Butane	4	22	2	2	2	2	t	t	2	—	—
	Butene-1	—	—	—	—	—	—	—	—	13	43	79
	Total, (l)	2.56	0.54	3.63	3.62	4.71	4.43	4.43	4.45	1.99	1.39	1.88
Liq. prod.	Butene-1	—	—	—	—	—	—	—	—	11 <sup>a</sup>	27 <sup>a</sup>	61 <sup>a</sup>
	Pentene-1	26	78	8	8	2	0.8	0.7	0.4	—	—	—
	1.5-Hexadiene	28	20	12	14	8	1.8	2.2	3.0	26	56	28

t trace amount.

<sup>a</sup>Percent yield, calculated from volume percent in the gaseous product.

non-catalytic conditions can be rationalized by an ethyl-crotyl exchange process between crotyl halides and ethylmagnesium bromide to form crotyl Grignard reagent. This line of argument may be extended to the catalytic function of metallic salts. Thus, low sensitivity of the diene composition to the catalysts and the increase of the diene in the order of I > Br > Cl in the catalytic reaction of crotyl halides (Table 2) might be explained by acceleration of such an exchange process by metallic salts. However, the considerable difference in the diene compositions with and without catalyst and especially the marked dependence on the nature of catalysts in the reaction with allyl chloride seem inconsistent with such a simple exchange process. Although intervention of such an exchange could not entirely be excluded, another pathway involving an allylic metal intermediate would be a more reasonable choice (vide infra).

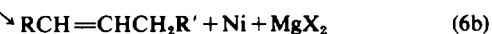
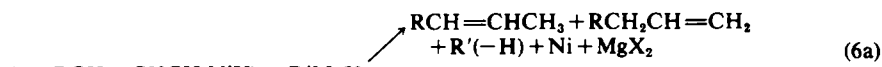
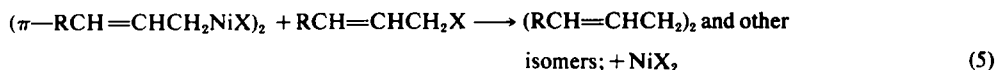
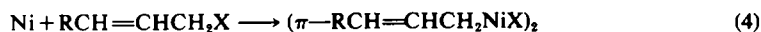
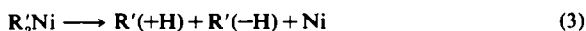
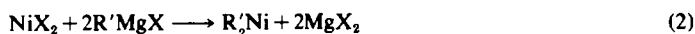
*Hydride shift from Grignard reagent to allylic halide.* When propylmagnesium bromide was used, crotyl chloride gave dienes in the similar yield in the presence of iron(III), copper(II) and cobalt(II) salts. However, some increase in the quantities of butene-1 and -2, which come from crotyl chloride through reduction are noticed by comparing Tables 2 with 4. With nickel chloride, a decrease of the diene accompanied by an increase of butenes is obvious. Coupled with the result obtained with methylmagnesium iodide in the presence of iron(III), the yields of dienes no doubt depend on the structure of the alkyl group in Grignard reagent, the increase in the yield being in the order of CH<sub>3</sub> > C<sub>2</sub>H<sub>5</sub> > n-C<sub>3</sub>H<sub>7</sub>.

In the previous communication,<sup>4</sup> formation of a large amount of propylene and butene-1 in nearly equal amounts was explained by hydrogen transfer

from n-butyl group of Grignard reagent to allyl chloride in the presence of nickel(II) or cobalt(II) salt. It is well known that reduction of carbonyl compounds in the Grignard reaction takes place by transfer of β-hydrogen as a hydride to carbonyl carbon. Although it is by a formal analogy to apply such a process to the present reaction of different nature, the results in Tables 2 to 5 seem to be well accommodated with the mobility of β-hydrogen in Grignard reagent. From this point of view, the previous result obtained in the Ni(II) or Co(II) catalyzed reaction of n-butylmagnesium bromide with allyl chloride (Table 3) may be considered to have been some of the extreme cases where such a hydrogen transfer was favorable. This consideration would lead to the possibility that a proper selection of Grignard reagent could make the reaction of allyl chloride to afford a good yield of cross- and homo-coupling products by suppression or exclusion of hydrogen transfer from Grignard reagent even in the presence of Ni(II) or Co(II) salt. This expectation was substantially realized in the reaction of methylmagnesium iodide where allyl chloride afforded a large amount of 1,5-hexadiene as well as butene-1, but only a trace of propylene even with nickel or cobalt catalyst.

*Mechanism.* By analogy with the view presented by Tamura and Kochi<sup>2</sup> on the nature of the active species in the Kharasch reaction, the reactive species in the present reaction are reasonably considered to be allylic metal intermediates. Thus, the present catalytic reaction would be essentially between the allylic metal intermediate and either allylic halide or Grignard reagent. For nickel and cobalt catalysts, the intermediate may be better described as π-allylic complex, since π-allylmetal bonding is well known for these transition metals.<sup>6</sup>

In the following argument the behavior of the intermediate will be discussed mostly with nickel catalyzed system, because the nature of  $\pi$ -allyl nickel complex has been well investigated. Corey *et al.*<sup>7</sup> reported that  $\pi$ -allylnickel complex affords dienes in the reaction with allylic halides or tosylates in good yields. This seems consistent with the results in Table 2 and does not contradict to those in Tables 3, 4 and 5, if the reaction of  $\pi$ -allylic nickel with Grignard reagent are taking place competitively. The latter reaction has not yet been described in the literature, but our preliminary work indicates that Grignard reagents carrying  $\beta$ -hydrogen in their alkyl moiety readily reduces  $\pi$ -allyl nickel bromide to propylene and metallic nickel, while the alkyl group of Grignard reagent is transformed into 1-alkene. Thus, the nickel catalyzed Kharasch reaction involving allylic halide could be described by the following reaction sequence, which may be also applicable to cobalt catalyst to some extent.



Distribution of the products would be determined by relative importance of the reactions (5), (6a) and (6b) for the particular reaction system. It is to be emphasized that the reaction (6a) or (6b) gives zero valent nickel and thus constitutes a kinetic chain in combination with the reaction (4) in the presence of excess allylic halide, while the reaction (5) produces nickel(II) halide which is to be reduced by Grignard reagent (reactions (2) and (3)) to repeat the catalytic cycle. This rationalization is consistent with the results obtained with nickel and cobalt catalysts in Tables 2 to 5, where increased yields of homo-coupling products are balanced by the formation of the alkane and the alkene (in comparable amounts) of Grignard reagent origin. The similar argument seems applicable to copper and iron catalyzed reactions, but the factors which contribute to the distribution of the products in the presence of these two catalysts are complex and difficult to evaluate at the present stage of knowledge, because these catalysts, especially copper(II) chloride showed a marked tendency to give cross-coupling product, and afforded a considerable amount of alkane in any of the present experiment.

Crotyl chloride as compared to allyl chloride favors the reaction (5) over reaction (4), the trend somewhat being offset by using a Grignard reagent with  $\beta$ -hydrogen of increased hydride character. The striking difference between the two halides (particularly with nickel and cobalt catalysts in Tables 2 and 5) suggests that an electronic effect of methyl substitution would not be a full explanation of the observed results.

#### EXPERIMENTAL

**Materials.** Commercial allyl chloride, crotyl chloride and bromide were purified by distillation. Crotyl iodide was prepared by reaction of crotyl alcohol with triphenyl phosphite metiodide<sup>8</sup> b.p. 50–53°C/40 mm Hg,  $n_D^{25}$  1.5554. Crotyldimethylphenylammonium iodide m.p. 113–114° (lit.<sup>9</sup> m.p. 113–114°). Anhyd transition metal chlorides were obtained by treatment of the corresponding hydrates of guaranteed quality with thionyl chloride under reflux for 2 hr and vacuum drying over KOH for over 12 hr.<sup>9</sup>

**Reaction procedure.** To a suspension of anhyd transition

metal chloride in anhyd ether under  $\text{N}_2$ , a filtered ethereal Grignard reagent (0.1 mol) was added and stirred under reflux until the evolution of gas ceased (reaction A). To the resultant dark soln, an equiv amount of allylic halide in ether was added and again stirred under reflux until the evolution of large amount of gas stopped (reaction B). The mixture was hydrolysed and treated in the usual manner; a liquid product was obtained by distillation of the dried ethereal extract. The product was analysed by gas chromatography using 2 m column packed with Silicone 703 (20%)–Celite 545 for crotyl halides. For allyl chloride, the ethereal soln containing added internal standard (cyclohexene) was directly injected on Gelay column HB 2000, 45 m. Composition of gaseous products in reaction A and B was determined using silica gel column (2 m) for methane, ethane and ethylene, and benzyl ether column (40%, 6 m) for other gaseous hydrocarbons.

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