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Effect of Transition Metal Chlorides in the Coupling of Allyl Chloride and *n*-Butylmagnesium Bromide[1)]

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Coupling reaction of allylic halides with Grignard and other organometallic reagents has been a subject of investigations[2)] and used as synthetic procedure. Contrary to the Kharasch reaction which involves the coupling of alkyl halides in a Grignard reagent solution in the presence of transition metal salts, the allylic coupling does not usually require any added catalysts. Probably because of this reason which certainly is attributable to the enhanced reactivity of the halides, there are few works which threw attention into a catalytic effect of added metal salts in the latter reaction.

In the previous paper[3)] we showed a considerable difference in their catalytic features among various metallic chlorides in the Kharasch coupling. This paper concerns with another example of a pronounced difference in activity among iron(III), copper(II), cobalt(II), and nickel(II) chlorides in the coupling reaction of allyl chloride with *n*-butylmagnesium bromide. To a solution of anhydrous metallic chloride suspended in anhydrous ether, a filtered ethereal *n*-butylmagnesium bromide (0.2 mol) was added and stirred under reflux until the evolution of gas ceased (reaction A) for 0.5 to 1 hr. To the resultant dark solution, an equivalent amount of allyl chloride in ether was added in a period of 10 min and again stirred under reflux for 3 to 5 hr (reaction B) until concurrent evolution of larger amount of gas stopped. After the reaction mixture was hydrolyzed and treated in a usual manner, distillation of the ethereal solution gave a mixture of liquid products. The compositions of gaseous products in reaction A and B, and the liquid products were analyzed by gas chromatography.

The effects of four metal salts in varying concentrations on the amounts of gas in reaction A and B, and the yields of the liquid products were illustrated in Figs. 1 to 4. The quantities of gas evolved in reaction A, indicative of the amount of the Grignard reagent utilized in the reduction of the metallic salts to lower valence states, were rather small and nearly independent on the kind of the metal salts when the relative concentration of the salts to the Grignard reagent are less than 10^{-2}. A pronounced difference, however, was observed in reaction B. When cobalt(II) and nickel(II) salts were used, a large amount of gas which were

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1) Reaction of Grignard Reagent Catalyzed by Transition Metal Salts. III.

2) a) S. Czernecki, C. Georgoulis, B. Gross, and C. Prevost, *Bull. Soc. Chim. Fr.*, **1968** 3713. b) R. M. Magid, E. C. Nieh, and R. D. Gandour, *J. Org. Chem.*, **36**, 2099 (1971) and references cited there. c) R. G. Gough and J. A. Dixon, *ibid.*, **33**, 2148 (1968).

3) Y. Ohbe and T. Matsuda, *Nippon Kagaku Zasshi*, **89**, 298 (1968).

Table 1. Comparison of the composition of the gas in reaction A and B for the four metal salts[a)]

		Co (II)		Ni (II)		Cu (II)		Fe (III)	
		1×10^{-4}	7×10^{-3}	1×10^{-4}	1×10^{-3}	1×10^{-3}	2×10^{-2}	3.3×10^{-3}	5×10^{-2}
A	Butane	81	121	178	233	140	177	164	321
	1-Butene	126	131	82	37	81	76	96	419
B	Butane	42	306	46	77	429	1523	425	900
	1-Butene	3510	3907	3180	3653	546	3420	765	2970
	Propylene	3740	3387	3130	3120	165	155	510	1080

a) 1 ML at 25 °C under atmospheric pressure.

consisted mainly of 1-butene and propylene resulted, but the yields of liquid products stayed at a low level throughout the catalyst concentrations adopted in this study. On the other hand, iron(III) and copper(II) salts showed an enhanced promoting effect in the coupling between allyl chloride and *n*-butylmagnesium bromide to afford 1-heptene as a major product with optimal concentrations of 5×10^{-3} equivalent for iron(III) and 1×10^{-3} for copper(II) salts. However, the reaction of allyl chloride with itself to give 1,5-hexadiene was little affected by the presence of any metal salt, and the yields remained at a low level irrespective of the nature of the added catalysts. Another information of interest was obtained by inspection of the compositions of gas in reaction B illustrated in Table 1 for the representative concentrations of each salts.

The major role of Grignard reagent in alkyl halide coupling under similar condition has been inferred[3)] to be regeneration of active catalytic species by reduction of the transition metal salts oxidized in the course of the coupling reaction, on the basis that the composition of the gas in reaction B was closely analogous to that of reaction A, which was consisted of alkane and alkene derived from the alkyl group of the Grignard reagent utilized. The striking contrast between the previous observation and the results in Table 1 could be rationalized as follows: (1) all four metallic chlorides are taking part in the reaction between allyl chloride and the Grignard reagent in their reduced forms, (2) cobalt(II) and nickel(II) chlorides promote exclusively the transfer of hydrogen from the alkyl group of the Grignard reagent to allyl chloride, thus, giving a nearly equal amount of propylene and 1-butene, and (3) substitution of the alkyl group is more favored in the presence of iron(III) and copper(II) chlorides (1a and 1b).

$$CH_2{=}CH{-}CH_2{-}Cl + CH_3(CH_2)_2CH_2MgBr$$

$$\swarrow \text{1a: } \begin{matrix}Co(II)\\ Ni(II)\end{matrix} \qquad \searrow \text{1b: } \begin{matrix}Fe(III)\\ Cu(II)\end{matrix}$$

$$\begin{matrix}CH_2{=}CH{-}CH_3 + \\ CH_2{=}CH{-}C_2H_5 + MgBrCl\end{matrix} \qquad \begin{matrix}CH_2{=}CH{-}(CH_2)_4{-}CH_3\\ + MgBrCl\end{matrix}$$

Although the amount of gas in reaction B markedly increased with iron(III) and copper(II) salts in the concentrations around 10^{-2}—10^{-1} equivalent, the results in Table 1 seems to suggest that the difference among two pairs of the salts is retained, especially in the case of copper(II) salt even in this concentration range. Alkyl metals have been recently proposed to be the active species in Kharasch coupling[4a)] and related reaction[4b)]. The present results could be accounted by assuming that these unstable species react with allyl chloride to form either ion-pair[2a)] or radical-pair[2c)] intermediate and the nature of carbon-metal bond of the alkyl metals determines which route favors 1a or 1b. However, a possibility of the intermediate

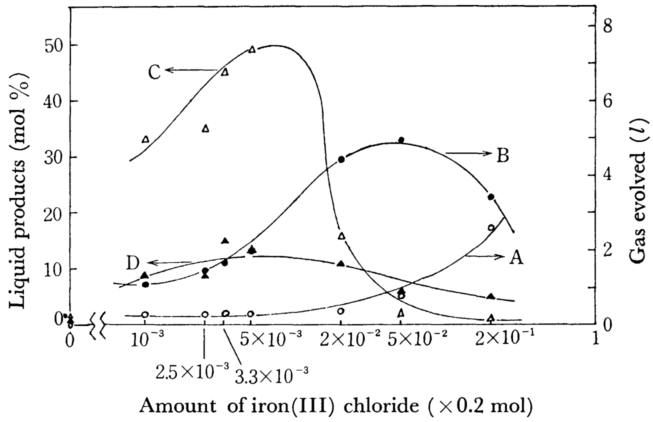

Fig. 1. Amounts of gaseous product in reaction A and B, and yields of liquid product.
A: A reaction gas, B: B reaction gas
C: 1-Heptene, D: 1,5-Hexadiene

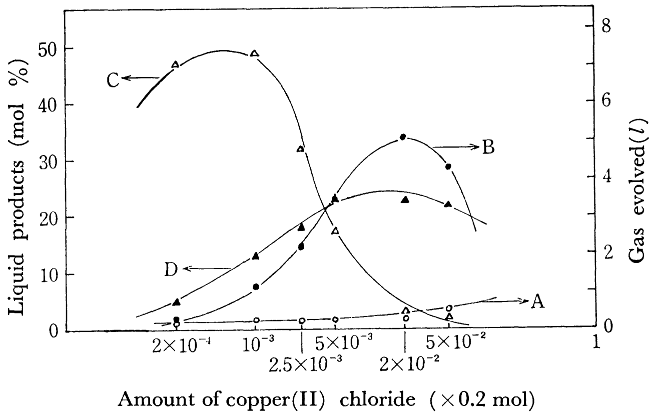

Fig. 2. Amounts of gaseous product in reaction A and B, and yields of liquid product.
A: A reaction gas B: B reaction gas
C: 1-Heptene D: 1,5-Hexadiene

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4) a) T. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970). *ibid.*, **93**, 1483, 1485 (1971). *J. Organometal. Chem.*, **29**, 111 (1971). *ibid.*, **31**, 289 (1971). b) T. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 1487 (1971).

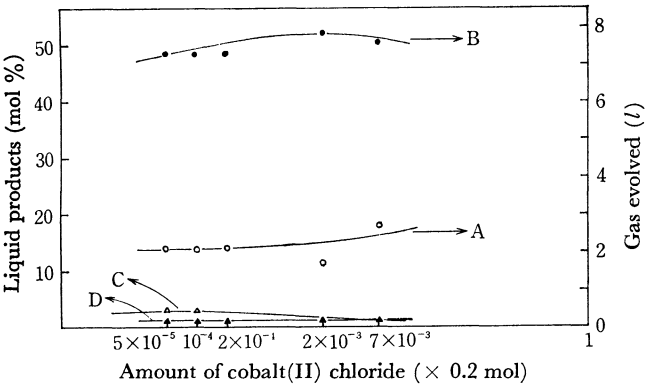

Fig. 3. Amounts of gaseous product in reaction A and B, and yields of liquid product.
A: A reaction gas B: B reaction gas
C: 1-Heptene D: 1,5-Hexadiene

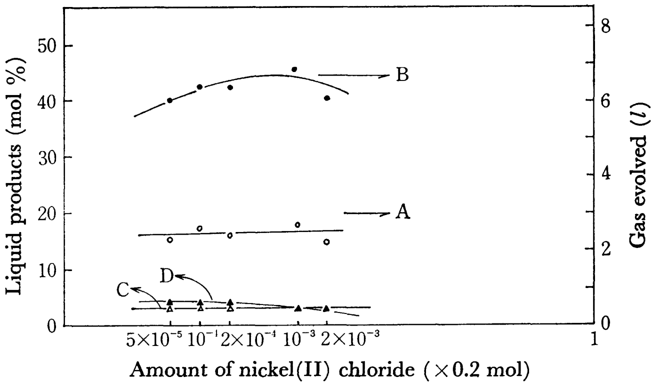

Fig. 4. Amounts of gaseous product in reaction A and B, and yields of liquid product.
A: A reaction gas B: B reaction gas
C: 1-Heptene D: 1,5-Hexadiene

formation of π-allylmetal species could not be entirely excluded in view of our preliminary observation that the reaction of crotyl halides with ethylmagnesium bromide afforded a mixture of three kinds of dienes which produced by coupling of the halide itself as principal product but little of hexenes, irrespective of the metallic chlorides utilized, and the chemical behavior[5] of π-allylnickel complexes which react rapidly with allylic halides and tosylates to give nonspecific cross coupling products.

Further studies are in progress to disclose the reason of the marked difference between allyl and crotyl halides and also a plausible structure of active intermediate.

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[5] E. J. Corey and M. F. Semmelhack, *J. Amer. Chem. Soc.*, **89**, 2755 (1967), E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *ibid.*, **90**, 2416 (1968).