Nitrate as an Oxidant in the Reaction of Silver(I) Salts with Grignard Reagents

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The reaction between various Grignard reagents and silver(I) salts in the presence of nitrogen-containing oxidants such as lithium nitrate, nitrogen dioxide, and methyl nitrate has been examined in tetrahydrofuran solutions. Coupling dimer is formed in high yields almost independently of the structure of the Grignard reagent. From the stoichiometry, it is concluded that these oxidants oxidize two equivalents of metallic silver formed *in situ* to silver(I) species under proper reaction conditions. Other transition metal halides are also oxidized by these oxidants in a similar manner. Soluble forms of reduced silver complexes formed in the reaction of silver(I) nitrate and Grignard reagent are also described.

The reactions of various transition metal salts and Grignard reagents in which alkane, alkene, and coupling dimer are obtained as products have been studied for some time.[1] Silver(I) salts are generally reduced to the metallic state in the presence of excess Grignard reagent, and the stoichiometry[2] of the reaction is generally represented by Eq. (2).

$$2\,\mathrm{RMgY} + 2\,\mathrm{AgX} \rightarrow [\mathrm{RH, R(-H), R{-}R}] + 2\,\mathrm{MgXY} + 2\,\mathrm{Ag} \qquad (1)$$

$$Q(\mathrm{R}) = \frac{\mathrm{R(-H)} + \mathrm{RH} + 2\,\mathrm{R{-}R}}{\mathrm{AgX}} = 1.0 \qquad (2)$$

The distribution of products is dependent on the Grignard reagent as well as the reaction conditions. The mechanism of the formation of coupling dimer has also been proposed.[3]

$$2\,\mathrm{R{-}Ag} \rightarrow \mathrm{R{-}R} + 2\,\mathrm{Ag} \qquad (3)$$

In most studies for this reaction, diethyl ether has been a medium of choice.[4]

We have examined the mechanism of the Kharasch reaction catalyzed by various transition metal salts and the reactions of transition metal halides with Grignard reagents, especially in tetrahydrofuran (THF) solution.[5] During these studies we found that nitrate is capable of acting as an oxidant in the *catalytic* reaction of silver(I) salt and Grignard reagent in THF.

In this paper we describe the reaction of silver(I) salt and Grignard reagent in the presence of nitrogen-containing oxidants such as lithium nitrate, nitrogen dioxide, and methyl nitrate in THF solutions. We also describe the soluble silver complex formed in the reaction of silver(I) nitrate and Grignard reagent in THF.

Results and Discussion

Reactions of Silver(I) Salts and Grignard Reagents. When a silver(I) salt was mixed with ethylmagnesium bromide in THF, *n*-butane was formed quantitatively together with a metallic silver precipitate as shown in Table 1.

$$2\,\mathrm{EtMgBr} + 2\,\mathrm{AgX} \rightarrow \mathrm{C_4H_{10}} + 2\,\mathrm{Ag} + 2\,\mathrm{MgBrX} \qquad (4)$$

Table 1. Reaction of silver(I) salts and ethylmagnesium bromide in tetrahydrofuran[a)]

AgX	Q(Et)	Distribution of product (%)			Alkali[c)] (mmol)
		C_2H_4	C_2H_6	n-C_4H_{10} [b)]	
AgBr	1.0	2.1	6.2	91.7	9.6
AgOAc	1.1	2.7	13.3	84.0	n. d.[d)]
$AgClO_4$	1.1	2.7	7.2	90.1	9.4
$AgNO_2$	1.5	2.7	21.9	75.4	n. d.[d)]
$AgNO_3$	3.6	1.4	11.2	87.4	10.5

a) In 21 m*l* THF solution containing 1.0 mmol AgX and 10.5 mmol EtMgBr at 25°C for 2.0 hr.
b) Percentage of n-C_4H_{10} was doubled.
c) Analysis after the reaction was completed.
d) Not determined.

A black precipitate was also formed immediately when silver(I) nitrate reacted with *excess* ethylmagnesium bromide. With this silver(I) salt, however, a part of the black precipitate gradually redissolved, accompanied by the formation of additional *n*-butane as shown in Fig. 1. Moreover, the value of Q(Et) in Eq. (2) was 3.6 in the case of silver(I) nitrate, which suggests that the nitrate acted as an oxidant during the reaction. The reactions of silver(I) nitrate and various organometallic compounds were also carried out in THF in order to see the general tendency of this unique behavior of nitrate. The results are summarized in Table 2 which shows clearly that Q(R) became greater than the usual stoichiometric requirements of 1.0, independently of the Grignard reagent. The coupling dimer was still the main product except

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[1] F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955); G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968); G. E. Coates, M. L. H. Green, and K. Wade "Organometallic Compounds" Vol. 2, Third ed., Methuen and Co., Ltd., London, (1968).

[2] C. D. M. Beverwijk and G. J. M. Van der Kerk *Organometal. Chem. Rev.*, **A5**, 215 (1970). J. H. Gardner *et al.*, *J. Amer. Chem. Soc.*, **51**, 3375 (1929); **59**, 2583 (1937); **61**, 2551 (1939); *J. Org. Chem.*, **61**, 2551 (1939). H. Gilman and J. M. Straley, *Rec. Trav. Chem. Pays-Bas*, **55**, 821 (1936).

[3] G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

[4] W. T. Miller *et al.*, *J. Amer. Chem. Soc.*, **90**, 7367 (1968); **91**, 6532 (1969); H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966) and references cited therein.

[5] M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 1483, 1485, 1487 (1971); M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, **29**, 111 (1971); **31**, 289 (1971); M. Tamura and J. K. Kochi, "Synthesis", 303 (1971); K. Wada, M. Tamura, and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970); M. Tamura and J. K. Kochi, This Bulletin, **44**, 3063 (1971).

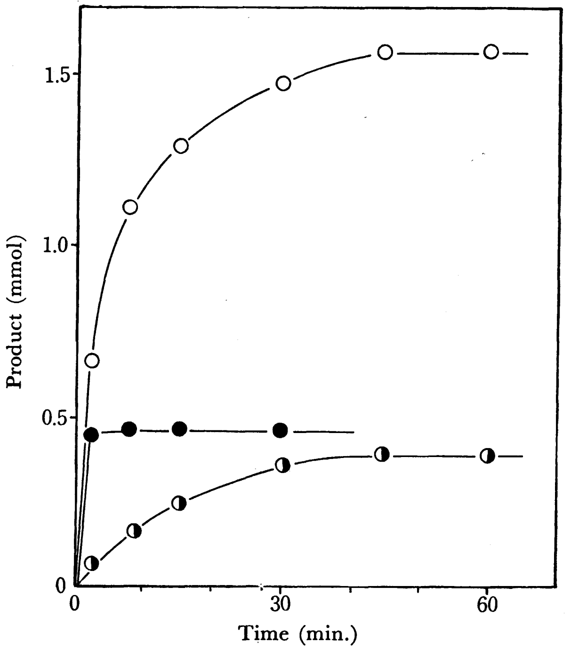

Fig. 1. Rate of formation of products in the reaction of silver(I) salts and ethylmagnesium bromide in tetrahydrofuran at 2°C.
THF: 21 m*l*, AgX: 1.0 mmol, EtMgBr: 7.3 mmol
○: *n*-C_4H_{10} from $AgNO_3$, ●: *n*-C_4H_{10} from AgBr
◑: C_2H_6 from $AgNO_3$

for secondary and tertiary alkyl Grignard reagents in which the formation of alkane and alkene predominated. *Q*(R) remained 1.0 when diethylzinc and triethylaluminum were employed, but no reaction took place between silver(I) nitrate and tetraethyllead or tetraethyltin.

Methyl, ethyl, *n*-propyl, isopropyl, and *t*-butylmagnesium bromides, ethylmagnesium chloride, diethylmagnesium, and ethyllithium all produced a black-brown solution (*vide infra*) in varying yields after the reactions were complete. On the other hand, phenyl, benzyl, and allylmagnesium bromides, diethylzinc and triethylaluminum did not afford brown solutions. Only a black precipitate and a colorless solution remained after the reaction was complete. These observations suggest that the formation of a black-brown solution is related to the reactivity of organometallic compound since benzyl and allylmagnesium bromides are more reactive, and phenylmagnesium bromide is less reactive than other alkyl Grignard reagents.[6]

The reaction of silver(I) nitrate and ethylmagnesium bromide was also greatly affected by the reaction temperature and the molar ratio of ethylmagnesium bromide to silver(I) nitrate as shown in Table 3. Thus, the value of *Q*(Et) and the yield of coupling dimer became larger at lower temperatures. The higher yields of soluble silver complex were obtained at lower temperatures and molar ratios of ethylmagnesium bromide to silver(I) nitrate of 5—7. The lower value of *Q*(Et) and the higher yield of ethane at higher temperature may be ascribed to the reaction of nitrate with ethylmagnesium bromide and the aggregation of metallic silver formed *in situ* (see Experimental, Table 6). *Q*(Et) also became greater than 1.0 when the reaction of silver(I) nitrate and ethylmagnesium bromide was carried out in diethyl ether, dioxane, and diglyme as indicated in Table 4. However, no soluble silver complex was formed in these solvents.

Reaction of Silver(I) Perchlorate and Ethylmagnesium Bromide in the Presence of an Oxidant. In order

TABLE 2. REACTION OF SILVER (I) NITRATE AND VARIOUS ORGANOMETALLIC COMPOUNDS[a)]

Organometallic compound	Temp. (°C)	Period (min)	*Q*(R)	Distribution of product (%)			Reaction[b)] mixture
				R(-H)	RH	R-R	
MeMgBr	2	120	1.0		3.1	96.9	A
MeMgBr	40	180	2.0		8.8	91.2	B
EtMgBr	2	60	3.4	1.2	9.2	89.6	B
EtMgCl	2	60	3.5	0.7	7.4	91.9	B
Et_2Mg	2	60	8.4	1.7	9.3	89.0	B
EtLi	2	60			n. d.		B
Et_2Zn	80	240	1.1	3.5	15.8	80.7	A
Et_3Al	40	60	1.1	7.6	20.0	72.4	A
n-PrMgBr	2	60	1.7	1.3	8.0	90.7	B
iso-PrMgBr	2	60	3.7	26.1	35.3	38.6	B
t-BuMgBr	2	60	3.8	38.7	38.7	22.6	B
CH_2=CHMgBr	2	60	1.6		5.1	94.9	A
CH_2=CHMgBr	25	60	3.5		6.8	93.2	B
PhMgBr	60	60	>1.7		n. d.	>90	A
$PhCH_2MgBr$	2	60	>2.9		n. d.	>90	A
CH_2=$CHCH_2MgBr$	2	60	3.4		8.3	91.7	A

a) In 21 m*l* THF solution containing 1.0 mmol $AgNO_3$ and 6.5—8.0 mmol organometallic compound.
b) Appearance of the reaction mixture after completion
A: Black precipitate and colorless solution
B: Black-brown solution (λ_{max} 415 nm) together with a black precipitate

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[6] J. H. Wotiz, C. A. Hollings, and R. Dessy, *J. Amer. Chem. Soc.*, **77**, 103 (1955).

TABLE 3. EFFECTS OF TEMPERATURE AND MOLAR RATIO OF ETHYLMAGNESIUM BROMIDE TO SILVER (I) NITRATE[a)]

EtMgBr/AgNO$_3$	Temp. (°C)	Q(Et)	Distribution of product (%)			Soluble Ag[b)] (%)
			C$_2$H$_4$	C$_2$H$_6$	n-C$_4$H$_{10}$	
7.3	62	2.4	3.8	48.7	47.5	1
7.3	25	3.5	2.6	21.3	76.1	24
7.3	2	3.3	1.8	10.1	88.1	34
7.3	−10	3.3	1.2	9.1	89.7	n. d.[c)]
14.6	2	3.3	1.2	9.0	89.8	2
5.1	2	2.8	2.2	13.8	84.0	32
2.9	2	1.9	2.1	14.9	83.0	18

a) In 21 ml THF solution containing 1.0 mmol AgNO$_3$ reacted for 60 min.
b) Percentage of soluble Ag in solution, based on AgNO$_3$ charged.
c) Not determined.

TABLE 4. EFFECT OF SOLVENT ON THE REACTION OF SILVER (I) NITRATE AND ETHYLMAGNESIUM BROMIDE[a)]

Solvent	Temp. (°C)	Period (min.)	Q(Et)	Distribution of product (%)			Reaction[b)] mixture
				C$_2$H$_4$	C$_2$H$_6$	n-C$_4$H$_{10}$	
Et$_2$O	2	90	1.8	2.7	22.7	74.6	A
Et$_2$O	25	90	1.6	3.7	34.2	62.1	A
Dioxane	25	60	1.5	6.1	38.5	55.4	A
Diglyme	2	60	3.3	3.0	12.6	84.4	C
Diglyme	20	60	2.4	3.3	18.2	78.5	C

a) In 21 ml solution (84 vol% solvent and 16 vol% THF) containing 1.0 mmol AgNO$_3$ and 7.3 mmol EtMgBr.
b) Appearance of the reaction mixture after completion.
A: Black precipitate and colorless solution
C: Brown precipitate and colorless solution

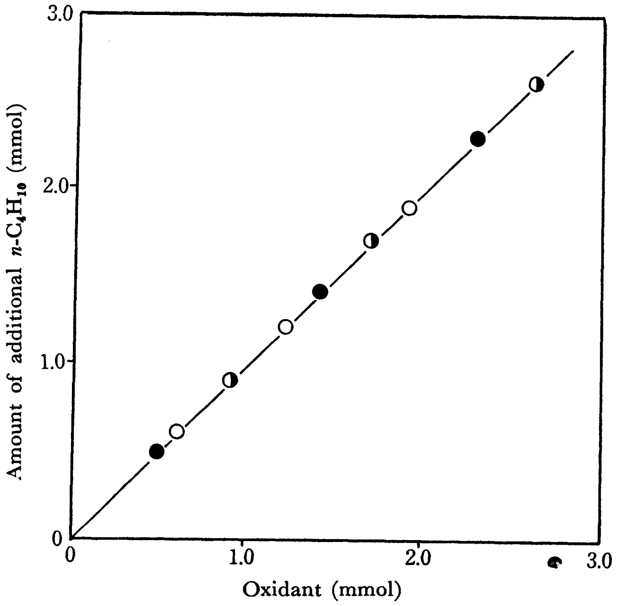

Fig. 2. Increase in the amount of n-butane from the reaction of silver(I) perchlorate and ethylmagnesium bromide in the presence of an oxidant in tetrahydrofuran at 2°C for 60 min. THF: 21 ml, AgClO$_4$: 1.0 mmol, EtMgBr: 8.7 mmol
●: Methyl nitrate, ○: Nitrogen dioxide, ◑: Lithium nitrate

to determine the role of nitrate as an oxidant, the reaction of silver(I) perchlorate and ethylmagnesium bromide in THF solutions was examined in the presence of other oxidants. When methyl nitrate, lithium nitrate, or nitrogen dioxide was added in the reaction, greater than stoichiometric amounts of coupling dimer was also formed as shown in Fig. 2. Furthermore, additional coupling dimer was formed when lithium nitrate was added to the black suspension resulting from the reaction of silver(I) bromide and excess ethylmagnesium bromide in THF. It is clearly indicated from the slope of the plot in Fig. 2 that these oxidants oxidize two equivalents of metallic silver.[7)]

$$\mathrm{AgClO_4 + EtMgBr \rightarrow 1/2\, C_4H_{10} + MgBrClO_4 + Ag} \quad (5)$$

$$\mathrm{2\,Ag \xrightarrow{Oxidant} 2\,Ag(I) \xrightarrow{EtMgBr} C_4H_{10} + 2\,Ag} \quad (6)$$

Similar results were obtained when silver(I) bromide replaced silver(I) perchlorate. Lithium nitrate and nitrogen dioxide also produced a black-brown solution, but methyl nitrate only afforded a black precipitate and a colorless solution. Sodium nitrite, nitric oxide, isoamyl nitrite, nitroethane and nitrobenzene, on the other hand, showed no evidence of enhancing the value of Q(R) beyond 1.0. The behavior shown by nitrate is, therefore, quite different from the result reported for the reaction of organocuprate with nitrobenzene.[9)]

The reaction between nitrate salts and Grignard reagents has not been published. It is known, how-

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[7)] One of nitrogen oxides (nitrogen dioxide *etc.*) formed *in situ* may be the essential oxidant. Oxidation of metallic silver with nitrogen dioxide may involve electron transfer since a small amount of nitric oxide was detected in gas phase during the reaction of silver(I) nitrate with ethylmagnesium bromide.[8)]

[8)] M. Tamura and T. Yasui, *Chem. Commun.*, **1968**, 1209; *Kogyo Kagaku Zasshi*, **72**, 575, 578, 581, 585 (1969).

[9)] G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

TABLE 5. REACTIONS OF TRANSITION METAL HALIDES AND ETHYLMAGNESIUM BROMIDE IN THE PRESENCE OF LITHIUM NITRATE[a)]

Transition metal halide	$LiNO_3$ (mmol)	EtMgBr (mmol)	Temp (°C)	Period (min)	Q(Et)	Distribution of product (%) C_2H_4	C_2H_6	n-C_4H_{10}	$\Delta Et^{b)}/LiNO_3$	Reaction[c)] mixture
$MnCl_2$		8.8	30	60	2.2	28.3	71.7	0.0		A
$MnCl_2$	0.95	18.0	30	360	7.0	37.6	61.1	1.3	5.0	B
$FeCl_3$		8.8	2	60	3.7	18.3	67.2	14.5		B
$FeCl_3$	0.50	18.0	2	60	6.8	18.5	37.4	44.1	6.0	B
$FeCl_2$		8.8	2	60	2.1	25.9	67.6	6.5		B
$FeCl_2$	0.95	18.0	2	60	6.3	19.6	37.0	43.4	4.3	B
$CoBr_2$		8.8	2	60	2.6	17.1	78.7	4.2		B
$CoBr_2$	0.95	18.0	2	60	7.2	32.5	55.4	12.1	5.4	B
$NiCl_2$		8.8	2	60	2.5	36.5	61.2	2.3		B
$NiCl_2$	0.95	18.0	2	60	6.1	28.3	50.8	20.9	3.8	B
$PdCl_2$		7.0	2	60	2.2	48.1	51.9	0.0		B
$PdCl_2$	0.95	18.0	2	150	5.0	42.4	56.2	1.4	3.1	B
CuCl		10.5	25	120	1.0	50.8	49.2	0.0		A
CuCl	0.95	18.0	30	60	3.5	19.9	47.7	32.4	2.6	B
$CuCl_2$		10.5	25	60	1.9	26.6	28.7	44.7		A
$CuCl_2$	0.95	18.0	25	60	4.3	18.6	32.5	48.9	2.4	B

a) In 21 m*l* THF solution containing 1.0 mmol transition metal halide.
b) Differences between the total yield in the presence of $LiNO_3$ and that in the absence of $LiNO_3$.
c) A: Black precipitate and colorless solution, B: Black-brown or brown solution together with varying amounts of precipitate.

ever, that various products are formed in the reactions of nitrogen dioxide, nitroalkanes, and organic nitrates with Grignard reagents.[10)] These reactions presumably involve addition of the Grignard reagent to the nitrogen-oxygen bond. Similar reactions are probably involved with nitrates since diethylhydroxylamine was obtained in the reaction of lithium nitrate and ethylmagnesium bromide in THF after hydrolysis (see Table 6).

Reactions of Transition Metal Halides and Ethylmagnesium Bromide in the Presence of Lithium Nitrate. The role of lithium nitrate as an oxidant was also examined in the reactions of other transition metal halides and ethylmagnesium bromide in THF solution. The results summarized in Table 5 show that lithium nitrate can act as an oxidant in varying degrees of efficiency.

$$MX_n \xrightarrow{\text{excess EtMgBr}} \text{Products} + M \qquad (7)$$

$$M \xrightarrow{\text{Oxidant}} M^{+m} \xrightarrow{\text{EtMgBr}} \text{Products} + M \qquad (8)$$

The higher efficiency was observed with manganous, ferric, ferrous, cobaltous, and nickelous halides since the values of $\Delta Et/LiNO_3$ were larger with these compounds.

Interestingly, the addition of lithium nitrate also afforded soluble metal species from manganous and cuprous(cupric) chlorides.

$$MX_n \xrightarrow{\text{excess EtMgBr}} \text{Products} + M \text{ (Black precipitate)} \qquad (9)$$

$$MX_n \xrightarrow{LiNO_3\text{-excess EtMgBr}} \text{Products} + \text{Soluble M species} \quad \text{(M; Ag, Cu, and Mn)} \qquad (10)$$

The effect of lithium nitrate on the formation of reduced metal species was not clear with other transition metal halides since soluble species were also formed from these transition metals in its absence.

The formation of coupling dimer from other transition metal halides was also facilitated by lithium nitrate. Its effect could not be examined directly since most ethyl transition metal complexes are labile.

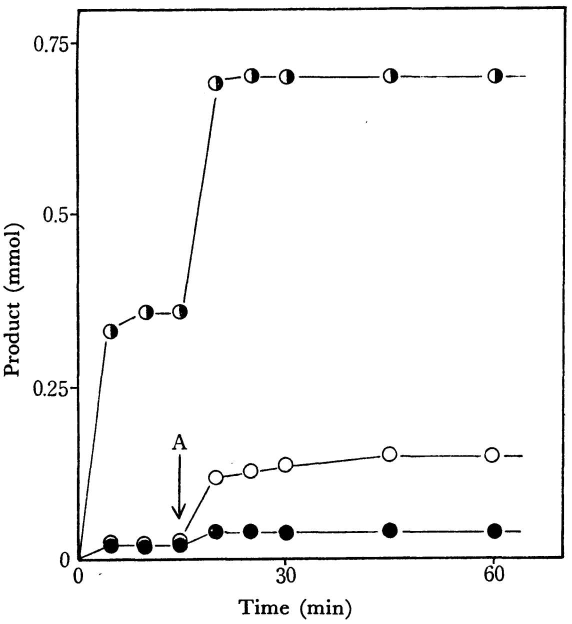

Fig. 3. Rate of formation of products in the reaction of cupric chloride and ethylmagnesium bromide in the presence of nitrogen dioxide.
In 21 m*l* THF solution containing 1.0 mmol $CuCl_2$ and 1.68 mmol EtMgBr at 2°C
◑: n-C_4H_{10}, ○: C_2H_6, ●: C_2H_4
Nitrogen dioxide (0.80 mmol) was added at point A,

[10)] M. S. Kharasch and O. Reinmuth, "Grignard Reagents of Nonmetallic Substances" Prentice-Hall Co., New York, N. Y. (1954).

Ethylcopper and ethylmanganese complexes, however, are relatively stable thermally in THF solutions.[5)] The rate of the reaction between ethylcopper and nitrogen dioxide is illustrated in Fig. 3 which shows that the coupling dimer was formed immediately in high yield.

$$2\,\mathrm{EtCu} \xrightarrow{\mathrm{NO_2}} \mathrm{Et\text{-}Et} + 2\,\mathrm{Cu\ species} \qquad (11)$$

Ethane and ethylene, on the other hand, were the principal products in the absence of nitrogen dioxide as indicated in Table 5. The oxidation of organocuprates with molecular oxygen to form coupling dimer has been reported in an analogous situation.[9)] We also find that the oxidation of ethylcopper species in THF with molecular oxygen affords *n*-butane in excellent yields. Oxidation of a mixture of ethylcopper and *n*-propylmagnesium bromide with nitrogen dioxide in THF yielded a mixture of three coupling dimers (*n*-butane, *n*-pentane, and *n*-hexane) in high yield.

$$\mathrm{EtCu} + n\text{-}\mathrm{PrMgBr} \rightleftarrows n\text{-}\mathrm{PrCu} + \mathrm{EtMgBr} \qquad (12)$$

$$\mathrm{EtCu} + n\text{-}\mathrm{PrCu} \xrightarrow{\mathrm{NO_2}} \mathrm{C_4H_{10}} + \mathrm{C_5H_{12}} + \mathrm{C_6H_{14}} + \mathrm{Cu\ species} \qquad (13)$$

Nitrogen dioxide also oxidized methyl and ethylmanganese species in THF solutions. Coupling dimer was obtained quantitatively from methylmanganese species, and equimolar amounts of ethane and ethylene were formed from ethylmanganese species.[5)]

These observations suggest that lithium nitrate increases the yield of coupling dimer by direct oxidation of the alkyl transition metal complex formed *in situ*.

Soluble Form of Reduced Silver Complex. A soluble silver complex was formed, as mentioned above, in the reaction of silver(I) nitrate with Grignard reagent, diethylmagnesium or ethyllithium and in the reaction of silver(I) perchlorate with ethylmagnesium bromide in the presence of lithium nitrate or nitrogen dioxide in THF. It was not formed in the reaction of silver (I) nitrate with phenyl, allyl, benzylmagnesium bromide, diethylzinc, or triethylaluminum or in the reaction of silver(I) perchlorate with ethylmagnesium bromide in the presence of methyl nitrate. The reaction temperature and the molar ratio of ethylmagnesium bromide to silver(I) nitrate also greatly influenced the yield of soluble silver complex (Table 3).

The soluble silver complex designated as (A) showed a sharp λ_{max}, at 415 nm after dilution of the reaction mixture with THF, and the absorption was independent of the organometallic compound (Table 2). When an excess of Grignard reagent was added to the silver complex(A), the λ_{max} was shifted to 400 nm to form a new species(B) as shown in Fig. 4.

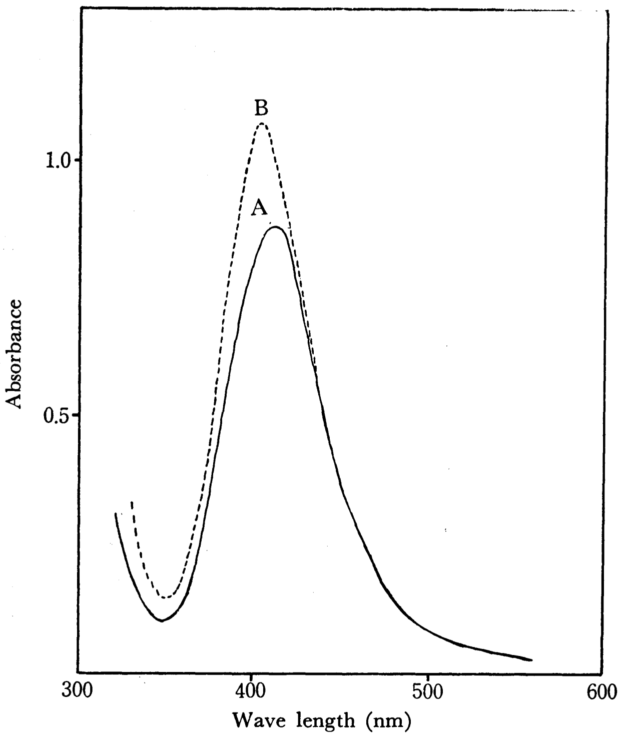

Fig. 4. Visible spectra of soluble silver complexes from the reaction of $AgNO_3$ and EtMgBr in THF.
Ag conc. 0.54×10^{-4} M, at room temperature
A: Reaction solution after dilution with THF
B: In the presence of excess EtMgBr

The chemical behaviors of the soluble complex(A) obtained from the reaction of silver(I) nitrate with diethylmagnesium are summarized in Fig. 5. The solution did not contain ethyl–metal groups since no ethane was evolved on acidic hydrolysis. Metallic silver was recovered quantitatively as a black precipitate when the solution was hydrolyzed with dilute sulfuric acid. Silver(I) species were absent since no silver(I) chloride was detected after extraction with concentrated ammonium solution followed by neutralization with hydrochloric acid. The soluble silver complex did not appear to react with excess triphenylphosphine and diethylzinc (no change in the visible spectra). The addition of benzyl and allyl bromides to the silver complex(A) afforded dibenzyl and diallyl, respectively, and silver(I) bromide in stoichiometric amounts. Oxidation of the soluble silver complex(A) with oxygen afforded silver(I) species only partially. When an equal amount of diglyme was added to the solution of complex(A), a black-brown precipitate was formed immediately. This precipitate was soluble in fresh THF and the resulting solution showed the same λ_{max} at 415 nm. The black-brown precipitate was washed with a 1 : 1 mixture of diglyme–THF under helium several times until no magnesium compound was detected in the washings. The solid, however, still contained magnesium compound in amounts corresponding to the ratio of silver/magnesium=1.1. The infrared spectra of the purified brown solid, which was dried *in vacuo* at room temperature, showed no characteristic absorptions. Both solutions of the complexes absorbing at 415 and 400 nm also showed no signal when the electron spin resonance spectra were examined.

We infer from these observations that both complexes (A) and (B) are composed of zerovalent silver. No zerovalent silver complexes have been cited.[11)]

[11)] R. R. Dewald, J. M. Brooks, and M. A. Trickey, *Chem. Commun.*, **1970**, 963.

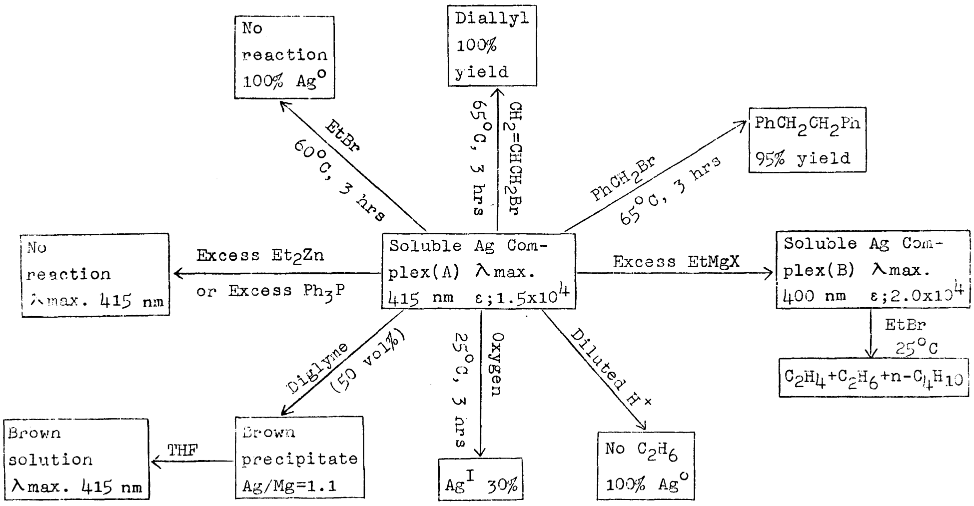

Fig. 5. Properties of the soluble silver complex obtained in the reaction of silver (I) nitrate and diethylmagnesium in tetrahydrofuran.

However, the formation of zerovalent cobalt and iron complexes coordinated with Grignard reagent have been reported under similar conditions.[12] Complex (B) absorbing at 400 nm may be a silver complex coordinated with Grignard reagent and is represented as the complex which shows enhanced catalytic activity in the Kharasch reaction.[5] The structure of complex(A) absorbing at 415 nm is not clear, but we assume that it is a zerovalent silver complex coordinated with one of the nitrogen-containing magnesium compounds formed in the reaction (see Experimental). Complex(B) absorbing at 400 nm was more stable than complex(A) absorbing at 415 nm and could be stored for prolonged periods in a refrigerator.

The lower yields of complex(A) obtained at higher temperatures and at higher molar ratios of ethylmagnesium bromide to silver(I) nitrate may be attributed to the aggregation of the silver species presumed to be the catalyst in the Kharasch reaction.[5] The relationship between the organometallic compound and nitrogen-containing oxidant on the yield of complex (A) may also be related to the aggregation of silver.

Experimental

All reactions in this paper were carried out under an inert atmosphere.

Materials. A billet of triply sublimed magnesium was obtained from Dow Chemical Co. Anhydrous nickelous chloride was prepared from the reaction of its hexahydrate and thionyl chloride. Anhydrous ferrous chloride was prepared by disproportionation of iron and anhydrous ferric chloride in THF.[13] Anhydrous manganous chloride was prepared from its tetrahydrate by treating at 150°C for 50 hr *in vacuo*. Anhydrous ferric chloride, palladous chloride, cobaltous bromide, cuprous chloride, cuppric chloride, silver(I) bromide, acetate, nitrate, nitrite and perchlorate, lithium nitrate, nitrogen dioxide, nitric oxide, isoamyl nitrite, and triphenylphosphine were of commercial grade and used without further purification. Nitrobenzene, nitroethane, and all organic bromides were purified by distillation before use. Methyl nitratew as prepared from methyl alcohol and nitric acid.[14]

Organometallic Compounds. All Grignard reagents were prepared as usual except for the use of 1.5 times excess metallic magnesium and low temperature (5∼25°C). After filtration under nitrogen, all solutions of the Grignard reagents (0.5∼2.0 M) were almost colorless except for vinylmagnesium bromide. The concentration of each Grignard reagent was determined by back titration with base and by the measurement of the amount of hydrocarbon liberated after acidic hydrolysis. Diethylmagnesium was prepared by precipitation of magnesium bromide from the Grignard reagent with dioxane followed by replacement of ether with THF. Ethyllithium (benzene solution, purchased from Lithium Corporation of America, Inc.) and triethylaluminum (supplied from Du Pont Co.) were of commercial grade. Diethylzinc was prepared from the reaction of zinc–copper couple with a mixture of ethyl bromide and ethyl iodide.[15] Tetraethyllead[16] and tetraethyltin[17] were prepared from the Grignard reagent in ether solution.

Solvents. THF was purified by refluxing over lithium aluminum hydride for 2 days, fractionating under nitrogen and stored under helium. Diethyl ether, dioxane, and diglyme were purified in a similar manner.

Analysis of Organic Product. Organic products were analyzed by gas chromatography using the internal standard method as previously reported.[5]

Analyses of Silver and Magnesium. Silver(0) was analyzed by titration[18] with a standard solution of potassium thiocyanate after extraction of silver(I) species with concentrated ammonium solution, filtration and oxidation with

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TABLE 6. REACTION OF NITROGEN-CONTAINING OXIDANT WITH GRIGNARD REAGENTS IN TETRAHYDROFURAN[a)]

Oxidant	mmol	Grignard reagent RMgBr	mmol	Temp (°C)	Period (min)	RH (mmol)	R loss[b)] (mmol)	Alkali[c)] (mmol)
$LiNO_3$	2.5	MeMgBr	15.4	23	120	0.10	~0	15.4
$LiNO_3$	2.0	MeMgBr	7.3	62	120	0.43	2.6	9.2
$LiNO_3$	1.2	EtMgBr	8.1	31	120	1.40[d)]	3.2	9.2
$NaNO_2$	2.0	EtMgBr	8.1	31	120	0.07	~0	8.1
$MeONO_2$	1.6	EtMgBr	7.0	2	60	0.47	n. d.[e)]	n. d.
NO_2	0.85	EtMgBr	7.0	2	60	0.70	n. d.	n. d.
$EtNO_2$	1.4	EtMgBr	7.3	2	60	0.95	n. d.	7.2

a) In 21 m*l* THF solution.
b) RMgBr charged minus total RH after hydrolysis.
c) Titrated after the reaction was completed.
d) Contained 0.28 mmol C_2H_4 and 0.09 mmol *n*-C_4H_{10}, A small amount of nitric oxide was detected in gas phase by gc (molecular sieve).
e) Not determined.

nitric acid. Silver(I) species was analyzed gravimetrically after precipitation as silver(I) bromide. Magnesium was determined by EDTA titration.[17)]

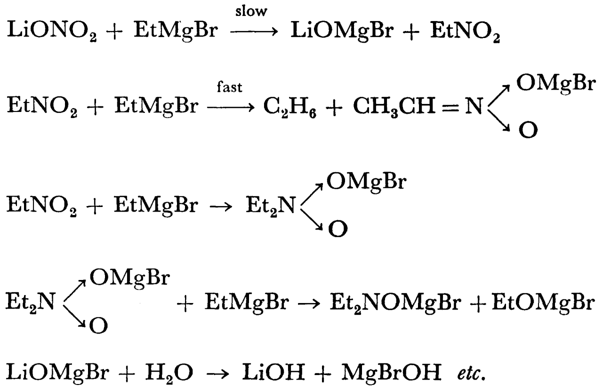
Reaction of Silver(I) Nitrate and Ethylmagnesium Bromide in Tetrahydrofuran (Typical example). To a 250 m*l* round bottomed flask equipped with a magnetic stirring bar and sealed with a rubber serum cap was added 0.17 g silver(I) nitrate. The nitrogen atmosphere was replaced with helium and 17 m*l* of THF was added with a syringe. After the flask was immersed in a dry ice–acetone bath, 25 ml of methane and 25 m*l* of isobutane (both markers) were added with syringes. The flask was then transferred to an ice–water bath. After 5 min agitation, 4.0 m*l* of ethylmagnesium bromide (7.3 mmol) was added to the solution with stirring. The color of the solution became black (suspension) immediately and then gradually changed to a black-brown solution. A small portion of the gas phase was removed with a hypodermic syringe and analyzed by gas chromatography at intervals of time. After the reaction was complete (60 min), a small portion of the reaction mixture was transferred to a deaerated test tube sealed with a serum cap. The mixture was centrifuged for 5 min and 0.10 m*l* of the black-brown supernatant solution was transferred to UV cell sealed with a rubber septum and containing 20 m*l* of THF. Visible spectrum was measured in the range 300~600 nm (λ_{max} 415 nm, Absorbance; 0.82). λ_{max} shifted to 400 nm (Absorbance; 1.35) when 1.0 m*l* of ethylmagnesium bromide solution (1.8 M) was added to the solution in UV cell. All subsequent reactions were also carried out in a similar manner.

Reaction of Nitrogen-Containing Oxidants with Grignard Reagents in Tetrahydrofuran. The reactions of nitrogen-containing oxidants with Grignard reagents were examined in THF solutions. The results are summarized in Table 6 which shows that the corresponding alkane was formed in varying yield. The reaction of lithium nitrate and methylmagnesium bromide did not proceed smoothly at 23°C but it occurred at 62°C to form predominantly methane. The reaction of sodium nitrite and ethylmagnesium bromide was also negligible. After the reaction was complete, the amount of alkali was greater than that of ethylmagnesium bromide charged.

The rate of formation of ethane in the reaction of lithium nitrate and ethylmagnesium bromide was also examined in THF solution. The amounts of ethane were determined at 5-min intervals and plotted against time. From the slope of the resulting line, the rate of formation of ethane was calculated (initial rate). A systematic variation of the concentration of each component led to the following empirical equation.

$$\frac{dC_2H_6}{dt} = k[LiNO_3]^{1.0}[EtMgBr]^{1.2}$$

The apparent activation energy of this reaction was 17.0 kcal/mol and the apparent second order rate constant was approximately 10^{-3} *l* mol^{-1}–sec^{-1} at 2.0°C. These results suggest that the following reactions occurred in the reaction between lithium nitrate and ethylmagnesium bromide.[10)]



$$LiONO_2 + EtMgBr \xrightarrow{slow} LiOMgBr + EtNO_2$$

$$EtNO_2 + EtMgBr \xrightarrow{fast} C_2H_6 + CH_3CH{=}N\langle^{\nearrow OMgBr}_{\searrow O}$$

$$EtNO_2 + EtMgBr \rightarrow Et_2N\langle^{\nearrow OMgBr}_{\searrow O}$$

$$Et_2N\langle^{\nearrow OMgBr}_{\searrow O} + EtMgBr \rightarrow Et_2NOMgBr + EtOMgBr$$

$$LiOMgBr + H_2O \rightarrow LiOH + MgBrOH\ \textit{etc.}$$

Diethylhydroxylamine was the main product isolated after acidic hydrolysis from the reaction between lithium nitrate and ethylmagnesium bromide as well as that between silver(I) nitrate and ethylmagnesium bromide. However, these reactions can not be directly related to the oxidant since neither nitroethane or diethylhydroxylamine acted as an oxidant during the reaction of silver(I) perchlorate and ethylmagnesium bromide. It is possible that one of the nitrogen oxides (nitrogen dioxide *etc.*) is the essential oxidant. The formation of nitrogen oxides in the reaction of lithium nitrate and ethylmagnesium bromide may involve electron transfer since nitrogen oxides are formed during the oxidation of metallic palladium with lithium nitrate in acetic acid.[8)]

Reaction of Silver(I) Nitrate and n*-Butylmagnesium Bromide in the Presence of Lithium Nitrate.* Silver(I) nitrate (2.5 mmol), lithium nitrate (20 mmol), and 50 m*l* THF were added to a 500 m*l* round bottomed flask which was previously flushed with nitrogen and sealed with a rubber serum cap. A solution of 1.0 M *n*-butylmagnesium bromide (100 m*l*) was added and the mixture was stirred for 3 hr at 10°C. The reaction mixture was worked up in the usual manner after addition of dilute sulfuric acid and extraction with petroleum ether. Distillation afforded 1.85 g (72% based on total nitrate group) of *n*-octane.

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