EFFECT OF SOLVENTS ON REACTIONS OF ORGANOMETALLIC COMPOUNDS

## II. EXCHANGE OF RADICALS BETWEEN RMgX AND R'X

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In a previous paper[1] we showed that interaction between organomagnesium compounds and alkyl halides in ethers of high solvating power results mainly in the formation of the products of a "normal" Wurtz reaction:

$$RMgX + R'X \longrightarrow R-R' + MgX_2$$
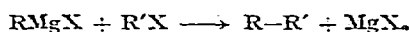
This was accompanied by the formation of hydrocarbons RR and R'R' together with hydrocarbons RR' and suggested that, during the reaction, the Grignard reagent and the added alkyl halide had exchanged alkyl radicals:

$$RMgX + R'X \rightleftarrows R'MgX + RX$$
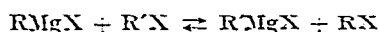
Using a $C_5H_{11}MgBr-CH_3I$ system in a solution of dimethoxyethane we have found that such an exchange of radicals does actually take place.

A suggestion that this kind of exchange is possible was made by Urion[2] in explanation of Grignard's "entrainment" method for the preparation of organomagnesium halides. However, most attempts aimed at detecting an exchange in the case of the simplest R and R' groups proved fruitless[3,4], although in some specific cases an exchange was observed[5-7]. It was also shown that an exchange reaction is accelerated by addition of transition-metal salts or by incorporating transition metals in the magnesium metal used in preparing the Grignard reagent[8]. Recently Korshunov and Batalov[9] reported on an exchange in a $C_2H_5MgBr-C_2H_5Br$ system in ether solution (12 h at 40°) although negligible exchange occurred between C_6H_5MgBr and C_2H_5Br.

Proceeding from our earlier suggestion that heterolytic reactions of organometallic compounds are facilitated by the presence of a strongly solvating solvent, we have investigated, in the present paper, an exchange between organomagnesium compounds and some alkyl and aryl halides in various ether media. We found that the rate of exchange depends substantially on the solvating power of the solvent. For instance, it was established that an exchange of alkyl radicals between *n*-amylmagnesium bromide and methyl iodide (Table 1) takes place to a small but significant extent in diethyl ether (5.7 % at 0–5° in 1 h). Under the same conditions, but in diethoxyethane, methoxyethoxyethane, diglyme, tetrahydrofuran and dimethoxyethane, exchange takes place to the extent of 6.6, 12.7, 15.8, 20.3 and 38.5 %, respectively. Under the conditions we have chosen, the exchange is accompanied to some extent by Wurtz's reaction as evidenced by the formation of ethane in small quantities. This means that the apparent extent of the exchange is somewhat lowered because the

methylmagnesium bromide produced is partly removed from the reaction mixture in the form of ethane.

TABLE 1

EXTENT OF EXCHANGE IN THE $C_5H_{11}MgBr-CH_3I$ SYSTEM IN VARIOUS ETHERS
(One hour at 0°)

No.	Solvent	% CH_3MgX
1	Diethyl ether	5.7
2	Diethoxyethane	6.6
3	Methoxyethane	12.7
4	Diglyme	15.8
5	Tetrahydrofuran	17.5
6	Dimethoxyethane	38.5

It is of interest to note that the order of these ethers in their capacity as solvents in exchange reactions parallels, in the main, their ability to form radical anions[10]. Dimethoxyethane is the most favoured medium and can ionize (at the expense of solvation) alkali metals[11].

Exchange reactions of organometallic compounds with alkyl halides are rather widely used, for instance, in the chemistry of organolithium compounds[12]; it is known that exchange between alkyllithiums and alkyl halides takes place more easily in ether than in hydrocarbons[13]. During a study of the kinetics of these reactions in ether–pentane mixtures[14] it was found that in ether at —70° equilibrium was attained within 30 min, whereas in a mixture of ether(40 %)–pentane(60 %) equilibrium could be achieved only after 200–500 min. The mechanism of such exchange, however, is not yet clear.

A feature of these exchange reactions is that during the reaction a formal exchange takes place between the carbanion of an organometallic compound $(R^{\delta-}-M^{\delta+})$ and the positively charged alkyl group of the alkyl halide $(R^{\delta+}-X^{\delta-})$. In the case of organolithium compounds, one can postulate[13] that, at the expense of positive polarization of a halide atom, exchange takes place between a lithium cation and a "positively charged" halide atom by nucleophilic attack on the alkyl halide by an anion of the organolithium compound. In the case of organomagnesium compounds, Kharasch and Reinmuth[14] point out in their excellent monograph that, apart from those exchanges with compounds containing the so-called "positive" halide atom (α-haloketones, 1-bromoacetylenes and some heterocyclic halides), an exchange between a Grignard reagent and a halogen derivative is a relatively rare reaction and occurs via a free-radical mechanism. They also maintain that available data concerning the uncatalyzed exchange $RMgX + R'X \rightarrow R'MgX + RX$ are "dubious, to say the least"[14].

The results obtained in the present work lead to the conclusion that the mechanism of exchange reactions for organolithium and organomagnesium compounds should be mainly very similar, and that the differences between them are due to the fact that organolithium compounds are stronger nucleophilic reagents than organomagnesium compounds and are consequently more suitable for exchange reactions. We believe that it is groundless to postulate that an exchange between organomagnesium compounds and those containing a "positively charged" halide atom takes place by various

definite mechanisms. That solvating solvents affect the exchange rate and that an exchange between organomagnesium compounds and alkyl halides is facilitated by increased solvating power of a solvent should be considered as arguments in support of the hypothesis that this reaction is of a heterolytic nature. The acceleration of an exchange with increasing solvating power of a solvent is due to stronger solvation of the cationic part of the Grignard reagent resulting in its greater nucleophilic activity.

One suggestion concerning the exchange mechanism assumes that the exchange passes through the four-center state (I), in which the anionic part of the organomagnesium compound induces a positive charge on the halogen atom of the alkyl halide:

$$R-Mg:nS \quad R^{\delta-}\cdots Mg^{\delta+}:nS \quad R \quad Mg:nS$$

$$(I)$$

$$(nS = n \text{ molecules of solvent})$$
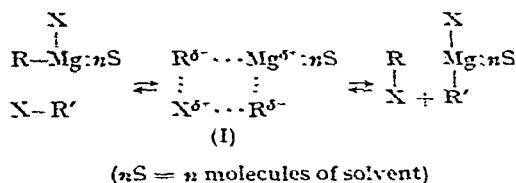
A magnesium atom passes through this transition state from a lesser electronegative radical to a greater electronegative one.

An alternative exchange mechanism is that the C–halide bond attacked by the nucleophilic part of the Grignard reagent is polarized so as to give rise to a positive charge on the halide atom, and an exchange proceeds via the transition state (II):

$$nS:Mg-R + R'X \rightleftarrows nS:Mg\cdots R\cdots X\cdots R' \rightleftarrows nS:MgR' + RX$$

$$(II)$$
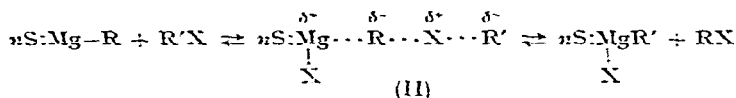
Such a polarization of the C–halide bond in this reaction is the reverse of that which occurs during Wurtz's reaction[1]:

$$nS:Mg\cdots R\cdots R\cdots X \longrightarrow RR' + MgX_2:nS$$
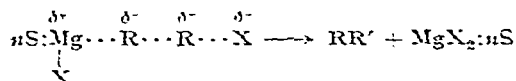
From this it should follow that the ease with which an exchange occurs is substantially dependent on the degree of the initial polarization, i.e., comparable electronegativities of radical R' and halide, and polarizability of the C–halide bond (deformability of a halide electronic shell). Since this markedly increases in the order Cl < Br < I and the electronegativity of halides with the same R' is in the same order, ease of exchange increases in the order R'Cl < R'Br < R'I.

At the same time, the character of the halide in the Grignard reagent should not greatly influence the ease with which an exchange takes place provided that the exchange of halide atoms according to RMgX + R'X ⇌ RMgX' + R'X is not significantly rapid.

To verify this assumption, we studied the influence of the halogen in an alkyl halide on the extent of exchange in the n-$C_5H_{11}Br$-C_2H_5Br system (Table 2; X = Cl, Br, I). As can be seen from this table, the extent of the exchange (0°, dimethoxyethane, 1 h) is negligible in the case of ethyl chloride, small in the case of ethyl bromide, but large in the case of ethyl iodide. Thus, exchange occurs much more easily in the case of alkyl iodides. The character of the halide in an organomagnesium compound

has practically no influence on the extent of exchange in the n-$C_5H_{11}MgX$–CH_3I system ($0°$, tetrahydrofuran, 1 h) (Table 2).

TABLE 2

INFLUENCE OF HALIDE IN ALKYL HALIDE AND ORGANOMAGNESIUM
COMPOUND ON THE EXTENT OF EXCHANGE IN THE RMgX–R'X' SYSTEM

No.	RMgX	R'X'	Solvent	% R'MgX
1[a]	$C_5H_{11}MgBr$	C_2H_5Cl	dimethoxyethane	0.2
2[a]	$C_5H_{11}MgBr$	C_2H_5Br	dimethoxyethane	1.0
3[a]	$C_5H_{11}MgBr$	C_2H_5I	dimethoxyethane	15.0
4[a]	$C_5H_{11}MgCl$	CH_3I	tetrahydrofuran	25.5
5[a]	$C_5H_{11}MgBr$	CH_3I	tetrahydrofuran	17.5
6[a]	$C_5H_{11}MgI$	CH_3I	tetrahydrofuran	20.3
7[b]	$C_5H_{11}MgBr$	C_6H_5Br	dimethoxyethane	0
8[b]	$C_5H_{11}MgI$	C_6H_5I	dimethoxyethane	52.0
9[b]	$C_5H_{11}MgBr$	p-BrC_6H_5Br	dimethoxyethane	0.8
10[b]	$C_5H_{11}MgBr$	p-ClC_6H_4Br	dimethoxyethane	12.0
11[b]	$C_5H_{11}MgBr$	p-ClC_6H_4I	dimethoxyethane	71.5
12[b]	$C_5H_{11}MgBr$	p-FC_6H_4Cl	dimethoxyethane	5.5
13[c]	$C_5H_{11}MgBr$	α-$C_{10}H_7I$	dimethoxyethane	74.4

[a] $0°$, 1 h; [b] $20°$, 3 h; [c] $20°$, 2 h; α-naphthoic acid was obtained (m.p. 159°), yield 74.4%.

The character of the halide also exerts a strong influence on the exchange reaction in the case of halobenzenes. Iodides react more easily than bromides and the extent of exchange increases if there is an electron-withdrawing substituent in the *para*-position.

No exchange occurs between bromobenzene and $C_5H_{11}MgBr$ ($20°$, 20 h) in contradistinction to the analogous reaction with alkyllithium, where such an exchange does not take place; this proves that RMgX, being a less powerful nucleophil than RLi, causes a less "positive" polarization of the C–Br bond in the transition state.

It should also be realized that the extent of exchange is strongly influenced by the electronegativity of the radical in the alkyl halide. The more electronegative the radical R' (other conditions being equal), the more it contributes to positive polarization of the halide, thus promoting the exchange. That this is so, is proved by the ease with which compounds containing potentially stable anionic groups attached to the halide (α-bromoketones, bromo- and iodo-acetylenes, perfluoroalkyl halides, etc.) undergo exchange. To draw up a comparison, in this respect, between common radi-

TABLE 3

THE DEPENDENCE OF THE EXTENT OF EXCHANGE
ON THE CHARACTER OF THE RADICAL R' ($0°$, 1 h)

No.	RMgX	R'X'	Solvent	% R'MgX
1	$C_5H_{11}MgBr$	CH_3I	tetrahydrofuran	17.5
2	$C_5H_{11}MgBr$	C_2H_5I	tetrahydrofuran	6.0
3	$C_5H_{11}MgBr$	n-C_3H_7I	tetrahydrofuran	2.5
4	$C_5H_{11}MgBr$	iso-C_3H_7I	tetrahydrofuran	2.5
5	$C_5H_{11}MgBr$	n-C_4H_9I	tetrahydrofuran	1.5
6	$C_5H_{11}MgBr$	$tert$-C_4H_9I	tetrahydrofuran	1.0
7	$C_5H_{11}MgBr$	$C_6H_5CH_2Cl$	tetrahydrofuran	1.0
8	$C_5H_{11}MgBr$	CH_3I	dimethoxyethane	20.7

cals, R', we also studied how the character of these radicals in alkyl halides influences the extent of exchange (Table 3).

We are fully aware that the qualitative estimation of the electronegativities of ordinary alkyl groups is extremely difficult, but we believe that the most reliable method available at present for this estimation is the experimental determination of N.Q.R. frequencies[16]. These data show that the methyl group in alkyl halides has much more electronegative character than its homologues; as a general rule the electronegativities of primary alkyl groups decrease with increasing chain-length. It might therefore be expected that exchange in the $C_5H_{11}MgBr$–RI systems would be maximal when R = CH_3 and would markedly decrease when changing to R = C_2H_5 and C_3H_7. The data we have obtained are in good qualitative agreement with these conceptions (Table 3): the greater the number of atoms in an alkyl halide the less is the degree of exchange observed.

Another trend, compatible with the electronegativity of the radical in the alkyl halide, which makes its influence felt is that an exchange reaction with a Grignard reagent proceeds in such a way as to produce an organomagnesium compound containing a more negative radical. It therefore becomes apparent why there is no exchange in the C_6H_5MgBr–CH_3I system (0°, 1 h, dimethoxyethane) since a phenyl group is more electronegative than the methyl group.

SUMMARY

(1) It has been found that an alkyl and aryl exchange between an alkylmagnesium halide and alkyl or aryl halides can take place in the case of the ordinary alkyl and aryl radicals, the reaction proceeding according to the scheme RMgX + R'X ⇌ R'MgX + RX.

(2) The rate of exchange of radicals between the alkylmagnesium halides and alkyl or aryl halides is dependent on the solvating capacity of the solvent and polarizability of the halogen in the alkyl halides.

(3) The mechanism of exchange between alkyl radicals is the same for both organomagnesium and organolithium compounds.

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