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THE EFFECT OF SOLVENTS ON REACTIONS OF ORGANO-METALLIC COMPOUNDS

THE INCREASING REACTIVITY OF ORGANO-MAGNESIUM COMPOUNDS IN SOLVATING MEDIA

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Dipolar aproton solvents are known in many cases to promote bimolecular substitution reactions of the type anion-dipole at the expense of increasing nucleophilicity of the anions. Parker[1] has reviewed the available evidence but disregarded organo-lithium, magnesium and aluminium compounds and a number of electron donating aproton solvents such as ethers, amines etc., which exhibit a strong solvating effect on these compounds. Organometallic compounds of this type apparently do not form independent carbanions but possess polar M—C bonds. We believe that the conception concerning the reactions of anions may be extended to substitution and exchange reactions involving the rupture of the M—C bond. With alkyl derivatives of lithium, magnesium and aluminium it is evident that the predominant solvation of the cationoid portion of the molecule is effected at the expense of the donor-acceptor interaction of the solvent and the electron unsaturated atom of the metal.

As solvation of these molecules is due to the electron unsaturation of the covalently bonded metal atom, there should, in principle, be no difference between pure solvation and the formation of stable complexes at the expense of unshared p-electron pairs of the solvent. It follows that energy of the heterolytic rupture of C—M bonds in solvates and complex compounds with ethers, amines etc, must be lower than that in the starting metal alkyls and, hence, they must display a higher nucleophilic activity. This assumption is supported by spectral evidence obtained by Brownstein *et al.*,[2] and points to the loosening of C—Al and C—Ga bonds in triethylaluminium and triethylgallium etherates as compared with free alkyl metals. Also in butyllithium, the C—Li bond is more readily ionizable in tetrahydrofuran than in hexane.[3]

In the reactions investigated, the more solvating (complexing) the medium, the higher the nucleophilic activity of the organometallic compound.

We believe that the effect of the solvent on the nucleophilicity of alkyl metals is governed by its solvating power and not, as often claimed by Hamelin and Normant, by its basicity.[4,5] The basicity in terms of the proton does not account for the

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[1] A. Parker, *Quart. Rev.* **16**, 163 (1962).

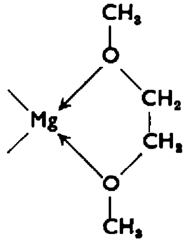
[2] S. Brownstein, B. S. Smith, G. Erlich and A. W. Laubengayer, *J. Amer. Chem. Soc.* **81**, 3826 (1959).

[3] R. Waack and M. Doran, *Chem. & Ind.* 1290 (1962).

[4] R. Hamelin, *Bull. Soc. Chim. Fr.* 684 (1961).

[5] H. Normant, *Bull. Soc. Chim. Fr.* 1434 (1963).

important role of spatial factors such as steric hindrance and the possible formation of energetically favourable cyclic structures of the type:



etc.

The discrepancy between the solvating power and basicity of the solvent is to some extent similar to the absence of correlation between the donating power of amines (in respect to borontrialkyls) and their basicity in water discovered by Brown[6] to be $NH_3 > EtNH_2 \gg Et_2NH > Et_3N$ and $NH_3 < EtNH_2 < Et_2NH \gg Et_3N$, respectively. The coordination power of aluminium hydride[7] decreases in the following series of complexing solvents: tetrahydrofuran > trimethylamine > diethyl ether. A similar series of solvents was obtained by the present authors while investigating exchange reactions in the systems RMgX–R'X and was found to decrease as follows: dimethoxyethane > tetrahydrofuran > triethylamine > diethyl ether.

The nucleophilicity of the C-metal bond may also increase when the electron deficiency at the metal atom is compensated by electrons from anions, as is the case in the series of organoaluminium complexes $MAlR_nHal_{4-n}$, etc. The suggestion that such complexes are more reactive than the corresponding free organoaluminium compounds has been reported in previous papers.[8,9]

We believe that purely solvating effects characteristic of weakly polar derivatives of heavy metals (Hg, Sn) and boron, silicon, etc. are a particular instance of the more general principle, that is, the increasing reactivity of the C—M (and similar) bonds under the action of coordination at the metal atom. A similar phenomenon is found in the reactions of "Nucleophilic assistance" the theory of which is being developed by Dessy and Paulik.[10,11] In the present report, experimental data substantiate these considerations.

We have studied, in particular, the effect of solvating solvents (of ether series) on the reactivity of organomagnesium compounds in substitution and exchange reactions.

It was anticipated that in solvents exhibiting a stronger solvating power than diethyl ether, organomagnesium compounds would be more active, the activity rising with the increasing cation solvating power of the solvent.

The increase in nucleophilicity of organomagnesium compounds in strongly solvating ethers (tetrahydrofuran, diglym, dimethoxyethane) has been observed in the following typical reactions:

(1) Würtz's reaction; (2) Exchange of $RMgX + R'X \rightleftharpoons R'MgX + RX$;

(3) Alkylation of the halides of elements; (4) Metallation of α-acetylenes.

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[6] H. Brown, *J. Amer. Chem. Soc.* **67**, 1452 (1945).

[7] R. Ehrlich, A. Young, B. Lichstein and D. Perry, *Inorg. Chem.* **2**, 650 (1963).

[8] L. I. Zakharkin, O. Yu. Okhlobystin and B. N. Strunin, *Zh. Prikl. Khim.* **36**, 2034 (1963).

[9] O. Yu. Okhlobystin, *Dissertation.* Moskov. Gosud. Univers., Moskva (1961).

[10] R. Dessy and F. Paulik, *J. Amer. Chem. Soc.* **85**, 1812 (1963).

[11] R. Dessy and F. Paulik, *J. Chem. Educ.* **40**, 185 (1963).

Although strongly solvating ethers have been repeatedly used in Grignard syntheses, their role in these reactions has not been fully elucidated. Their positive effect was thought to be due either to their higher dissolving power or to the higher temperature at which the reaction may be performed.

The solvents tried were ethers of ethylene- and diethyleneglycol, tetrahydrofuran and diethyl ether. Even in the preparation of simple alkylmagnesium halides it has been observed that the use of solvents such as dimethoxyethane promotes the Würtz's reaction,[12] and this is not common to Grignard reagents. In particular, in dimethoxyethane methylmagnesium iodide is not produced because methyl iodide reacts more readily with the organomagnesium compound already formed than it does with magnesium:

$$CH_3I + Mg \longrightarrow CH_3MgI \xrightarrow[DME]{CH_3I} C_2H_6 + MgI_2$$

A number of other examples have also demonstrated that the use of dimethoxyethane, one of the strongest solvating ethers, favours considerably the Würtz's reaction.

Normant has reported[5] that this reaction is promoted by the presence of strongly solvating or "more basic" solvents. It is to be noted that tetrahydrofuran[13] and, to a greater extent, dimethoxyethane[14] cause the "symmetrization" of alkylmagnesium halides (especially iodides). It has also been found that alkyl exchange reactions of simple organomagnesium compounds with halides (particularly iodides) proceed with ease in strongly solvating ethers:[15]

TABLE 1
(70°, 4 hr, dimethoxyethane)

No.	RMgX	R'X	Yield R-R'
1.	CH_3MgI	CH_3I	90·0
2.	C_2H_5MgBr	CH_3I	54·8
3.	C_3H_7MgBr	CH_3I	68·5
4.	C_3H_7MgBr	C_2H_5Br	49·3
5.	C_6H_5MgBr	C_2H_5Br	47·3

$$RMgX + R'X \rightleftharpoons R'MgX + RX$$

The degree of exchange (under comparable conditions) is proportional to the solvating power of the solvent, increasing in the series: diethyl ether < diethoxyethane < methoxyethoxyethane < diglym < tetrahydrofuran < dimethoxyethane.

These reactions show that there is no fundamental difference between exchange reactions in the series of organolithium and magnesium compounds, as was thought previously,[16] for the few and peculiar cases where the radical exchange between alkylmagnesium and alkyl halides had been unambiguously determined.

[12] L. I. Zakharkin, K. A. Bilevitch and O. Yu. Okhlobystin, *Dokl. Acad. Nauk SSSR* **152**, 338 (1963).

[13] R. Hamelin and S. Hayes, *Bull. Soc. Chim. Fr.* 692 (1961).

[14] H. Cohen and G. Wittig, *J. Org. Chem.* **18**, 432 (1953).

[15] L. I. Zakharkin, O. Yu. Okhlobystin and K. A. Bilevitch, *J. Organometal. Chem.* **2**, 309 (1964).

[16] M. S. Kharash and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances* p. 1060, Prentice-Hall, New York (1954).

These results suggest, that organomagnesium compounds would also display higher reactivity in other heterolytic reactions such as the alkylation of the halides of elements.

In Grignard reactions, such as the alkylation of thallium trichloride which proceeds only to the dialkylthallium halide stage unless by the addition of alkyllithium trialkylthallium is obtained,

$$R_2TlCl + RLi \rightarrow R_3Tl + LiCl$$

it is found that the simple addition of tetrahydrofuran results in the easy substitution of chlorine in diethylthallium chloride to give triethylthallium in a 48·5% yield:

$$(C_2H_5)TlCl + C_2H_5MgBr \xrightarrow{THF} (C_2H_5)_3Tl + MgBrCl$$

A similar reaction in ether results in the reduction of the organothallium compound up to metallic thallium.

Similarly, treatment of trichlorosilane with α-naphthylmagnesium bromide does not give rise to tri-α-naphthylsilane which is obtained only by means of α-naphthyllithium.[17] Nametkin *et al.*[18] by the use of tetrahydrofuran as solvent, obtained tri-α-naphthylsilane in a 29·7% yield, but with a stronger solvating solvent such as dimethoxyethane, it is possible, even under mild conditions, to obtain a 71% yield of α-naphthylsilane.

$$HSiCl_3 + 3\alpha\text{-}C_{10}H_7MgBr \xrightarrow{DME} (\alpha\text{-}C_{10}H_7)_3SiH + 3MgBrCl$$

This solvent has been used successfully also in the preparation of pentaphenylantimony synthesized by Wittig[19,20] via phenyllithium.

$$Ph_3SbCl_2 + 2PhMgBr \xrightarrow{DME} Ph_5Sb + MgBrCl$$

Alkylation of trimethylchlorosilane with phenylethynylmagnesium bromide requires heating to 100° for 3 hours (after removal of ether),[21] but in tetrahydrofuran or dimethoxyethane the reaction is exotermic at room temperature, the yield of trimethylphenylethynylsilane being to 47 and 77·2%, respectively.

The rise in nucleophilicity of alkylmagnesium halides is as marked in the preparation of Iotsich complexes. The simple substitution of tetrahydrofuran for ether in the preparation of bis-(bromomagnesium)-acetylene results in the reaction becoming exothermic, the rate being controlled by the rate of addition of acetylene to the reaction mixture.

Reporting on the preparation of ethylmagnesium bromide in tetrahydrofuran Jones *et al.*[22] noted only the higher solubility of acetylene but did not mention the increased activity of ethylmagnesium bromide.

The interaction rate of methylmagnesium bromide and phenylacetylene in different ethers at 0° depends essentially on the solvating power of the medium. In

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[17] H. Gilman and R. Clark, *J. Amer. Chem. Soc.* **69**, 1499 (1947).

[18] N. S. Nametkin, T. I. Chernysheva and K. K. Krechetova, *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk* 2219 (1963).

[19] G. Wittig, *Liebigs Ann.* **577**, 26 (1952).

[20] G. Wittig and M. Rieber, *Liebigs Ann.* **562**, 186 (1949).

[21] A. D. Petrov, L. L. Schukovskaya and Yu. P. Petrov, *Dokl. Akad. Nauk SSSR* **93**, 293 (1953).

[22] E. Jones, L. Skattebol and M. Whitting, *J. Chem. Soc.* 4765 (1956).

diethyl ether the reaction is very slow whereas in tetrahydrofuran and dimethoxyethane the half life of methane is 9·4 and 6·0 minutes, respectively. Dessy[23] while investigating the interaction of various Grignard reagents with acetylenes, did not report any change in the reaction rate on addition of tetrahydrofuran to the ether solution of ethylmagnesium bromide since he regarded changes in the basicity of the medium as the rate determining factor.

In strongly solvating solvents such as dimethylformamide, aliphatic organozinc compounds also readily metallate acetylenes.

The influence of complexing on the reactivity of the C—M bond is clearly exhibited in the alkylation of halides using alkylaluminium. In these exchange reactions, use is often made of sodium and potassium chloride,[9,24,25] as well as of t-amines and ethers,[26] which permit milder reaction conditions. It is considered that as a result of these additions the aluminium halide forms an inactive complex e.g. $NaAlCl_4$, $AlCl_3 \cdot NR_3$, etc.

In the light of the experimental data given it is more likely that the complex compounds $NaAlR_3Cl$, $R_3Al \cdot NR_3$, etc contain Al—C bonds which are more polar and hence more active in exchange and substitution reactions than the starting alkylaluminium compounds.

It has been found that under conditions when trimethylaluminium hardly react with silicon tetrachloride, the presence of potassium chloride promotes the production of tetramethylsilane. This is also the case in the alkylation of methylphenyldichlorosilane with triisobutylaluminium. Complexing agents have previously been used in the preparation of tin and germanium derivatives[8,9] by means of alkylaluminium. In addition to the above considerations, the complexed aluminium halide has more ionic Al—Hal bonds, which are less favourable to back dealkylation than $AlHal_3$ itself. It is the combination of these factors that enhances the reaction course in the presence of complexing compounds.

It is to be noted, however, that the advantages are essentially valid only for substitution (or exchange) reactions. The problem of the solvation effect on the course of addition reactions requires special analysis and proof, because the interaction of π-electrons of multiple bonds with the metal atom which is undoubtedly of importance in addition reactions, may be suppressed in the case of strong solvation and preliminary complexing. This accounts for the decreased reactivity of organomagnesium compounds with increasing coordination in reactions involving nitriles and other unsaturated compounds.

In general, a clear distinction should be made between the reactivity of organometallic compounds in heterolytic substitution (or exchange) reactions and, on other hand, in addition reactions to multiple bonds.

EXPERIMENTAL

1. *Triethylthallium.* A filtered solution of EtMgBr (from 0·1 mole EtBr) in 70 ml tetrahydrofuran was added to a suspension of Et_2TlCl (24·2 g, 0·081 mole) in 130 ml tetrahydrofuran at 0–5°

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[23] J. Wotiz, C. Hollingsworth and R. Dessy, *J. Org. Chem.* **20**, 1545 (1955).

[24] Brit. Patent 802796.

[25] J. van Egmond, M. Jensen, J. Luiten, J. van der Kerk and J. van der Want, *J. Appl. Chem.* **12**, 17 (1962).

[26] W. Neumann, *Liebigs Ann.* **653**, 157 (1962).

during 40 min, heated up to 20°. After removal of the solvent, the Et_3Tl was distilled, yield: 48·5%, b.p. 43°/1 mm.

2. *Pentaphenylantimony.* To 8·62 g Ph_3SbCl_2 in 75 ml dimethoxyethane at 10°, a solution of PhMgBr (from 0·08 mole Mg) in 30 ml ether was added. The mixture was stirred at 20° for 8 hr and decomposed by addition of water and a small amount of HCl aq. The organic layer was separated and the aqueous layer extracted with benzene. The combined solution was washed with water and dried over $MgSO_4$. After removal of the solvent the residue was crystallized from cyclohexane, yield of Ph_5Sb 6·8 g (61·7%), m.p. 157–159°.

3. *Tri-α-naphthylsilane.* To 0·1 mole α-$C_{10}H_7MgBr$ in 80 ml of a mixture of dimethoxyethane and tetrahydrofuran (1:1) at 10–15°, 2·98 g (0·022 mole) $HSiCl_3$ in 10 ml dimethoxyethane was added. The mixture was stirred for 4 hr at 20° and poured into NH_4Cl aq. The white crystalline deposit was washed with water, a mixture of dimethoxyethane–hexane and with hexane to obtain 6·4 g (71%) tri-α-naphthylsilane, m.p. 231–233°. After crystallization from alcohol the yield was 5·0 g (55·5%), m.p. 238–239°.

4. *Phenylethynyltrimethylsilane.* To a solution of $PhC{\equiv}CMgBr$ (from 0·1 mole phenylacetylene and 0·1 mole EtMgBr in 70 ml dimethoxyethane) 9·77 g trimethylchlorosilane was added at a rate to maintain the temp at 30–35°. The mixture was stirred for 4 hr and decomposed with water. The organic layer was separated and the aqueous layer extracted with ether. The combined solutions were washed with water and dried over $MgSO_4$. After separation of the ether, the residue was distilled *in vacuo* to yield 11·8 g (77·2%) phenylethynyltrimethylsilane, b.p. 85°/6 mm; n_D^{20} 1·5286. The reaction similarly conducted in tetrahydrofuran, yielded 47% phenylethynyltrimethylsilane.

5. *Tetramethylsilane.* A mixture of 20 g Me_3Al, 23 g $SiCl_4$ and 20 g KCl was heated in a steel ampoule to 190–200°. The crude tetramethylsilane (8·2 g) was distilled off directly from the ampoule and treated with water, alcoholic KOH and again with water to yield 4·8 g (40%) tetramethylsilane, b.p. 26·5–27·0°; n_D^{20} 1·3430; d_4^{20} 0·6462.