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Dual Reactivity of Arylmethylmetal Compounds

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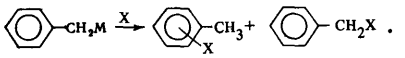
The review deals with the dual reactivity of ambident anions of arylmethylmetal compounds. Data on the mechanism of reactions of these compounds are described and the effect of various factors on the mode of reaction is discussed. The bibliography includes 93 references.

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I. INTRODUCTION

The reaction of benzylmagnesium chloride with trioxymethylene leading to the formation of β-phenylethyl alcohol was described in 1903.[1] In the same year it was reported[2] that the product of this reaction is *o*-tolylmethanol and that benzylmagnesium chloride therefore exhibits dual reactivity in its reaction with trioxymethylene:



The first stage in the study of the dual reactivity (or the so called "anomalous" reaction of arylmethylmetal compounds) was the determination of the generality of the reaction. It was found that, together with organomagnesium compounds, arylmethyl derivatives of other Group I (potassium[3], sodium[4], and lithium[5]), Group II (zinc[6-8], cadmium[6], and mercury[9,10]), and Group III (aluminium[6] and boron[11-14]) metals react similarly. The dual reactivity was observed not only in relation to carbocyclic but also heterocyclic compounds, namely derivatives of furan[15], thiophen[16-18], and their benzo-analogues[19]. The range of electrophilic reagents entering into the aromatic ring proved to be extremely wide, including aldehydes, ketones, various acid derivatives (esters, nitriles, anhydrides, and acid halides), carbonic acid derivatives (carbon dioxide, ethyl chlorocarbonate, phosgene, dicyanogen, and dithiocyanogen), alkyl halides, sulphuric acid esters, deuterium chloride, heavy water, etc. It was found that, together with the more usual *ortho*-substitution, in many cases *para*-substitution takes place and in a few reactions this is in fact the dominant process.

Some of the data obtained up to 1954 and dealing with reactions of organomagnesium compounds are summarised in Chapter XI of the monograph by Kharash and Reinmuth[20], who quote exhaustive factual data and put forward certain hypotheses concerning the reaction mechanism. Then, for a time, the reaction was hardly investigated. In the monograph by Ioffe and Nesmeyanov[21], only two isolated special studies[22,23] were added to those discussed in the previous review[20]. However, in recent years, interest in this reaction has been renewed, as can be seen from a considerable number of investigations dealing with the dual reactivity of arylmethyl compounds of both magnesium and other metals. The data which have now accumulated permit a general account of the dual reactivity of arylmethylmetal compounds and the determination of the general characteristics of the relevant reaction and of the effect of various factors on its course. The present review is an attempt at a general account of this kind.

II. REACTION MECHANISM

Tiffeneau and Delange, who were the first to describe the dual reactivity of benzylmagnesium chloride, already stated [referring to the corresponding reaction] that "this is a condensation of the same type as in the formation of primary aromatic alcohols by the reaction of formaldehyde with arylhydroxylamines or sodium phenoxide"[2]. In fact all investigators treat unamimously the "anomalous" reaction of arylmethylmetal compounds as a special case of electrophilic substitution in the aromatic ring activated as a result of the conjugation of the electrons of the carbon–metal σ-bond and the ring π-electrons†[24]. This conjugation accounts for the unusually high (compared with the effect of the methyl group) electron-donating effect of the CH_2M group, which is comparable to that of powerful electron-donating agents such as the amino- and hydroxy-groups (Table 1). The σ-π conjugation in the molecules of arylmethylmetal compounds explains their capacity to form *ortho*- and *para*-substitution products, but does not account for the finding that *ortho*-isomers predominate in the reaction products. Moreover the main product of the reactions of arylmethylmetal compounds is the *ortho*-isomer and the formation of the *para*-isomer may be regarded as exceptional. Selective *ortho*-substitution has been the starting point of the study of the reaction mechanism. Different related mechanisms, proposed to account for the dual reactivity of organomagnesium compounds[25-30], can be represented in a general form by Scheme 1 (c.f. Kharash and Reinmuth[20]) using as an example the interaction of benzylmagnesium chloride with formaldehyde.

Table 1. σ⁺ constants of the substituents[14,27].

Substituent	σ+	Substituent	σ+
Me	−0.311	CH_2HgCH_2Ph	−1.14
OH	−0.92	NH_2	−1.3
CH_2BX_2OH*	−1.11		

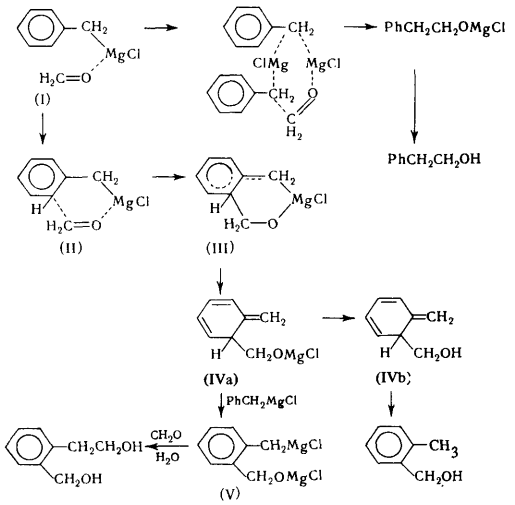
* X = acid residue

†The discussion which arose between Schmidlin[25], who attempted to justify the existence of two isomeric forms of benzylmagnesium compounds, and Chichibabin[26], who supported the idea of a dual reactivity of this compound, is of historical interest.

The first stage of the reaction is the formation of a Werner complex (I), which can react with a further molecule of benzylmagnesium chloride to form a quasi-six-membered ring, the decomposition of which leads to phenylethyl alcohol.

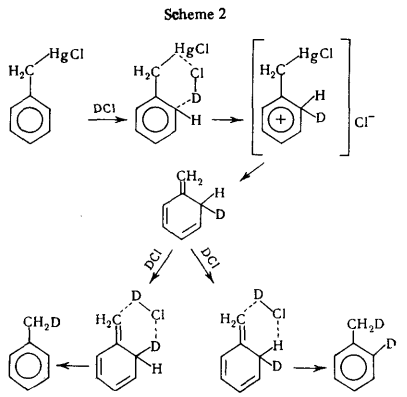
To account for the "anomalous" course of the reaction, one postulates the formation of an oriented π-complex (II), which is subsequently transformed into a σ-complex (III) and then into an *o*-metallated derivative of methylenecyclohexadiene (IVa). Hydrolysis of the latter results in the formation of methylenecyclohexadiene (IVb) the aromatisation of which leads to the final *ortho*-substitution product. Methylcyclohexadiene (IVa) can be metallated by an excess of the organomagnesium compound to form a new organomagnesium compound (V), which again reacts with formaldehyde.

Scheme 1



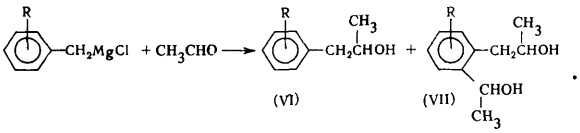
A similar scheme was proposed[31] to account for the dual reactivity of benzylmercury chloride (see Scheme 2).

Scheme 2



One must suppose that similar mechanisms can be put forward to account for the dual reactivity of the arylmethyl derivatives of other metals too. Scheme 2 is close to the mechanisms of electrophilic aromatic substitution reactions, for example the Kolbe reaction or the reaction involving the *ortho*-hydroxymethylation of phenols.

The individual stages of the proposed mechanism have been examined in various investigations and their occurrence with formation of intermediates has been demonstrated. Thus the formation of the oriented π-complex (II) as an essential stage in the formation of *ortho*-substituted products has been elegantly confirmed by Bernardon and Bourdais[32], who investigated the reaction of acetaldehyde with substituted benzylmagnesium chlorides:

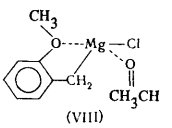


The reaction resulted in the formation of both the normal addition product, the secondary alcohol (VI), and of the "anomalous" diol (VII). The ratio of the yields of these products depends on the nature and position of the substituent in the phenol ring (Table 2).

Table 2. Effect of the substituent on the yield of products of the reaction of benzylmagnesium chloride and acetaldehyde.

Compound	R	Yield, %	Compound	R	Yield %
VI	H	10	VII	H	50
	o-OMe	70		*o*-OMe	0
	p-OMe	12		*p*-OMe	45
	o-Me	0		*o*-Me	85

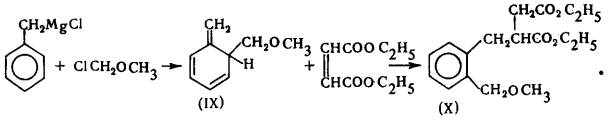
In the reaction involving *o*-methoxybenzylmagnesium chloride, the ring *ortho*-substitution product is not formed. Comparison with the reactions of *p*-methoxy- and *o*-methylbenzylmagnesium chlorides does not explain this phenomenon on the basis of the electronic or steric effects of the *o*-methoxy-group. The authors believe that the complex (I) formed in the reaction with *o*-methoxybenzylmagnesium chloride has structure (VIII), which rules out the formation of a π-complex and an *ortho*-substitution product.



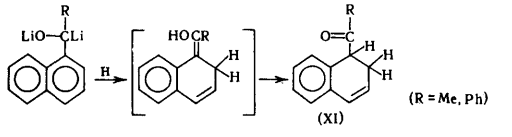
On the other hand, the steric effect of the *ortho*-methyl group favours the formation of a π-complex, the absence of the alcohol (VI) from the products being related to this factor. It is interesting to note that at an even earlier stage the absence of dual reactivity in ferrocenylmethyllithium was attributed to the impossibility of the formation of a cyclic transition state[33].

The formation of methylenecyclohexadiene in the course of reactions of arylmethylmetal compounds has been frequently postulated. The formation of considerable and sometimes predominant amounts of diaddition products is always explained by its presence. Bearing in mind the stability of methylenecyclohexadiene itself[34], its formation in the course of the reaction appeared extremely probable. Convincing proof of this was obtained[35-37]. In order to detect the methylenecyclohexadiene derivatives formed in the course of the reaction of benzylmagnesium chloride,

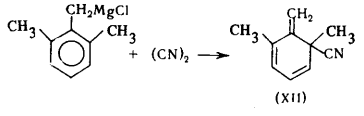
active substances, capable of reacting with these intermediates, were added to the reaction mixture. Thus the reaction mixture, obtained by allowing benzylmagnesium chloride to react with α-chloromethyl ether, was treated with diethyl maleate or maleic anhydride. The detection of diethyl α-(*o*-methoxymethylbenzyl) succinate (X) proved the existence of compound (IX):



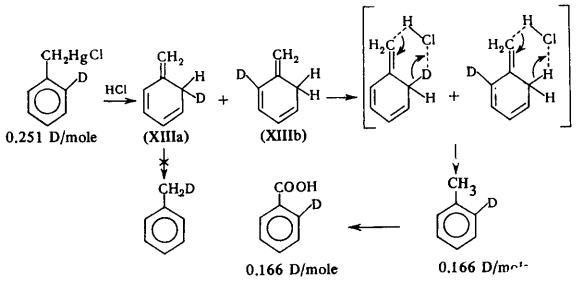
In a few cases, when the compounds with the methylenecyclohexadiene structure are stablised by additional factors, their formation may be demonstrated by spectroscopic methods. Thus, when α-hydroxyarylmethylmetal compounds of the naphthalene series were protonated, the formation of the diene system (XI) was demonstrated[38]:



Finally, compound (XII), formed in the reaction between 2,6-dimethylbenzylmagnesium chloride and dicyanogen, was isolated[39]:

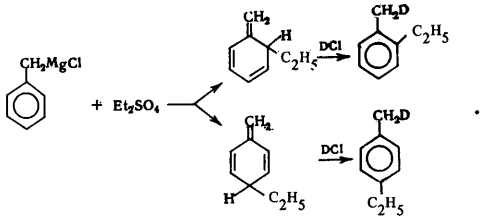


The data presented confirmed the hypothesis of the formation of methylenecyclohexadiene compounds in the course of the reaction. The problem of the aromatisation of the intermediates is somewhat more complex. At first sight it may appear that the simplest aromatisation pathway involves intramolecular proton migration. However, Kharash already pointed out that the aromatisation takes place intermolecularly, this being confirmed by a study of the reaction of *ortho*-tritiated benzylmagnesium chloride with formaldehyde[20]. The intermolecular mechanism of the aromatisation was proved[31]. in the reaction involving the protonation of and elimination of mercury from *ortho*-deuteriated benzylmercury chloride:

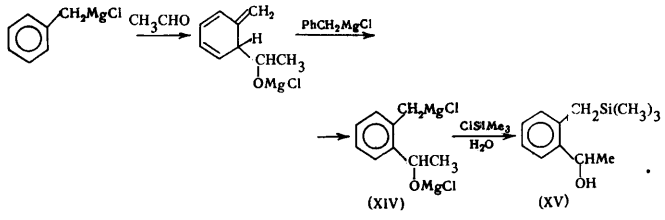


The lower deuterium content in toluene compared with the initial benzylmercury chloride is evidence of intermolecular aromatisation of compounds (XIIIa) and (XIIIb). The identical deuterium contents in toluene and in the benzoic acid obtained as a result of its oxidation suggest that the entire deuterium is located in the benzene ring, which could not occur in the intramolecular migration of the proton in compounds (XIIIa) and (XIIIb).

The intermolecular mechanism of the aromatisation of the methylenecyclohexadiene intermediates is also confirmed by the formation of deuteriated ethyltoluenes when the reaction mass obtained in the alkylation of benzylmagnesium chloride with diethyl sulphate is decomposed by deuterium chloride[37]:



It is also possible to postulate another pathway to the aromatisation of methylenecyclohexadiene compounds in this reaction: their interaction with an excess of the organometallic compound, the formation of a secondary organometallic derivative, and its reaction with deuterium chloride. However, not even traces of alkylation products of the secondary organomagnesium compounds could be detected in this case. The formation of the secondary organometallic product was demonstrated in another instance — in the interaction of benzylmagnesium chloride with acetaldehyde, which results in the formation of appreciable amounts of a diaddition product. The addition of the alkylating agent $ClSi(CH_3)_3$ to the reaction mixture yielded the alcohol (XV) — the alkylation product of the secondary organomagnesium compound (XIV):



Since the aromatisation of methylenecyclohexadiene compounds takes place via an intermolecular mechanism, it follows that the process (and hence the yield of the corresponding reaction products substituted in the aromatic ring) should depend on the nature of the neutralising agent. Experiments confirmed this conclusion[36]. Neutralisation of the reaction mass in the reaction of benzylmagnesium chloride with α-chloro-methyl ether by a strong acid (HCl) leads to higher yields of the "anomalous" products than neutralisation by a weaker acid (ammonium chloride). In the latter case there is apparently insufficient time for the dihydro-products to be aromatised and to undergo any changes (e.g. dimerisation[39]) in the course of subsequent isolation. On the other hand, the yield of the normal reaction product remains almost constant regardless of the agent employed.

The above mechanism covers also cases of *ortho*-substitution. There are no literature data on the basis of which a mechanism for *para*-substitution might be devised. One can suppose that, whereas *ortho*-substitution takes place via the interaction of one molecule of the nucleophilic agent with one molecule of an electrophilic agent, the *para*-substitution reaction requires the involvement of a larger number of molecules. One may point to the closely analogous instances where products of the 1,2-, 1,4-, and 1,6-addition of a Grignard reagent to conjugated systems are formed[40, 41]. Whereas 1,2- and 1,4-addition can be accounted for by a mechanism involv

the coordination of the metal to the carbonyl and the formation of a quasi-six-membered ring, the involvement of several molecules of the Grignard reagent is postulated to account for the 1,6-addition.

III. FACTORS INFLUENCING THE MODE OF REACTION

1. Electronic Structure of Arylmethylmetal Compounds

Examination of the mechanism of the reactions of arylmethylmetal compounds permits an approach to the consideration of the problem of factors affecting the mode of reaction. Although in the majority of studies on the chemistry of arylmethylmetal compounds, the influence of conditions on their reactivity has been demonstrated, there is no unanimous view in the literature on the causes responsible for changes in the mode of reaction. The number of studies specially undertaken on this question is small and the great sensitivity of the reaction to slight (at first sight) changes in conditions frequently makes it difficult to compare the results of different investigators. Comparable data have been taken as a rule from one investigation or from several investigations carried out under identical conditions.

We believe that it is valid to consider the reactions of arylmethylmetal compounds as process involving ambident anions. An ambident anion is one with two reaction centres combined into a single conjugated system. The factors responsible for the dual reactivity of ambident anions have been investigated and described in a series of reviews[42-44]. However, most studies dealt with the behaviour of ambident anions the reaction centres of which are of different chemical types. Usually one of these is a carbon atom and the other a heteroatom, or both centres are different heteroatoms. The negative charge is distributed between the two centres in such a way that most of it concentrated at the more electronegative atom; the second atom is as a rule more polarisable.

The benzyl anion and in general arylmethyl anions constitute a special case of ambident‡ anions of the allylic type. Its characteristic feature relative to other ambident anions (particularly relative to the phenoxide ion which has an isoelectronic structure) is that both nucleophilic centres are carbon atoms, although in different states of hybridisation. As in heteroambident anions, the negative charge is distributed between both centres. According to modern hypotheses, by virtue of the low amount of *s*-character of the hybridised orbital, the unsaturated sp^2-hybridised carbon atom is more electronegative than the saturated atom[45]. Therefore, to a close approximation, one may assume that the negative charge is largely concentrated on the carbon atoms of the aromatic ring. However, the formal sp^3-state of the methylene carbon atom in the benzyl anion does not of course correspond to its true state. The delocalisation of electrons in the carbon-metal bond should lead to partial rehybridisation of the α-carbon atom. In the limiting case, this atom should also be sp^2-hybridised and all the bonds should be equalised. The actual state of the α-carbon atom is intermediate and depends on the structure of the compound, the nature of the metal and the solvent, and other factors.

The question of the state of the methylene carbon atom in certain organolithium compounds of the arylmethyl series was investigated recently with the aid of ^{13}C NMR spectroscopy[46-48]. The ^{13}C chemical shift is an effective measure of the hybridisation and charge density. The average chemical shift of the sp^2-hybridised ^{13}C atom is 60 – 70 p.p.m. and that of the sp^3-hybridised ^{13}C atom is 160 – 170 p.p.m. For a given constant hybridisation of the carbon atom, the ^{13}C shift δ is proportional to the electronic density at the carbon atom, as can be seen from a comparison of the chemical shifts in methane and methyllithium or cyclopentadiene and cyclopentadienyl-lithium (Table 3)[46,49]. An increase of electron density in such cases leads to a shift of the signal towards a lower field. In contrast, on passing from arylmethyl hydrocarbons to their lithium derivatives, δ decreases, which can only be due to a change in the hybridisation of the α-carbon atom from sp^3 to sp^2. The data in Table 3 show that the hybridisation of the methylene carbon atom in the monophenylmethyl compound is closer to sp^3 than for the di- and tri-phenylmethyl compounds.

Table 3. Effect of the charge on the ^{13}C chemical shift.

Compound	δ $^{13}C(CS_2)$	$\Delta\delta$ ^{13}C	Compound	δ $^{13}C(CS_2)$	$\Delta\delta$ ^{13}C
CH_4	196		Ph_2CH_2	157	
MeLi	209	13	Ph_2CHLi	114	—43
C_5H_5	—4*		PhMe	172	
C_5H_5Li	26*	30	$PhCH_2Li$	163	—9
Ph_3CH	132				
Ph_3CLi	102	—30			

* Relative to benzene.

Table 4. Negative charge densities at different positions in the aromatic ring of arylmethylmetal compounds according to NMR spectroscopic data.

Compound	Charge density			References
	ortho-	*meta-*	*para-*	
Ph_3CLi	0.000	0.080	0.130	50
Ph_2CHLi	0.080	0.070	0.160	50
$Ph_2C(C_8H_7)Li$	0.041	0.079	0.162	54
$Ph_2C(C_8H_{11})Li$	0.040	0.077	0.158	51
$(Ph_2CCH_2)_2Li_2$	0.015	0.070	0.155	52
$(Ph_2CCH_2)_2Na_2$	0.000	0.060	0.145	52
$(Ph_2CCH_2)_2K_2$	0.020	0.065	0.155	52
$(MePhCCH_2)_2K_2$	0.205	0.120	0.295	52
$PhCH_2Li$	0.120	0.100	0.180	50
2-$PyCH_2Li$	0.160	0.150 (4.6)	0.220	53

The charges at different positions in the benzene ring arising as a result of the delocalisation of electrons of the C - M bond were found from the ^1H NMR spectra of the organometallic compound (Table 4). For certain compounds, the charges were also calculated by the LCAO-MO and SCF methods[50], the result of the calculation by the SCF method agreeing satisfactorily with the experimental data. The charges on the central carbon atom were not determined experimentally. Their calculation, based on the assumption that the charge of the anion is -1, is

‡ In fact the benzyl anion is not an ambident but a polydent species; however, for the sake of simplicity we shall regard it as an ambident anion with two nucleophilic centres — the methylene carbon atom and an aromatic carbon atom without distinguishing the *ortho-* and *para*-positions.

inaccurate because the total negative charge is not located on the organic part of the molecules owing to the interaction between the cation and the anion.

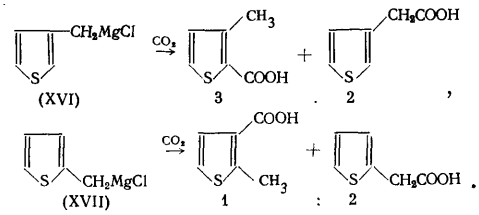
Although all the data quoted for the distribution of electron density in arylmethylmetal compounds refer to alkali metal derivatives, one may suppose that the situation is similar for other metal derivatives. Thus the spectrum of dibenzylmercury indicates the presence of fractional charges in the *ortho*- and *para*-positions in the benzene ring[55].

Thus the charge distribution in the molecules of arylmethylmetal compounds accounts for the attack of electrophilic agents both on the methylene carbon atom and on the aromatic part of the molecule. The mechanism of substitution in the aromatic ring discussed above in fact constitutes a special case of electrophilic substitution. It is evident that any factors promoting electrophilic substitution will increase the yield of ring-substituted products and will correspondingly diminished the yield of α-substituted products.

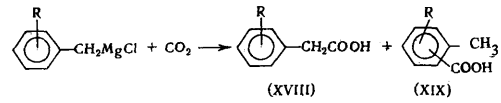
Experimental data show that an increase of electron density at any carbon atom of the aromatic ring facilitates the reaction at this centre of the ambident anion. Sherman and Anstutz[15] were already able to compare successfully various aryl residues in the reaction of arylmethylmagnesium chlorides with carbon dioxide. The yield of ring-substituted products increases in the series benzylmagnesium chloride < 2-thienylmethylmagnesium chloride < 2-furfurylmagnesium chloride. When electronegative groups are introduced into the aromatic ring, the conjugation between the C–M bond electrons and ring π electrons should increase with a corresponding increase of electron density at the carbon atoms of the aromatic ring, which facilitates the introduction of the electrophilic agent.

On passing from monocyclic compounds to their benzoderivatives, the yield of ring-substituted products increases. This was observed for the first time for heterocyclic compounds[19] and was then demonstrated in a comparison of benzyl and naphtylmethyl derivatives[23, 56]. Reactions of organometallic derivatives of 2-methylnaphthalene lead to 3-substituted and not 1-substituted derivatives, which may be related to a lower energy of charge localisation when the electrophilic agent attacks the 1-position[56, 57].

It is interesting to compare the two organometallic compounds (XVI) and (XVII). Owing to the $+I$-effect of the sulphur atom, substitution in the ring of the β-isomer (XVI) takes place to a greater extent than in the ring of the α-isomer (XVII)[58]:



It is evident that substituents in the benzene ring should have similar effect also on the dual reactivity of arylmethylmetal compounds. Since electron density in the *ortho*- and *para*-positions relative to the methylene group is important for the ring-substitution reaction, electron-donating groups in the *meta*-position should have the greatest effect. This has been confirmed by a study[59] of the carboxylation of various substituted benzylmagnesium chlorides:



(XVIII) (XIX)

A study of the effect of ring substituents on the kinetics of simultaneous deuteriation and demercuration of benzylmercury chloride provided convincing evidence for the effect of electron-donating *meta*-substituents[61, 62]. The products of this reaction contain considerable amounts of deuterium in the ring, which suggests a dual reactivity.

Table 5. Effect of the substituent in the benzene ring on the dual reactivity of benzylmagnesium chloride.

Compound	R	Yield, %	Compound	R	Yield, %
XVIII	H	100	XIX	H	0
	o-Me	100		*o*-Me	1
	p-Me	90		*p*-Me	10
	m-Me	30		*m*-Me	64*

* 2,4-dimethylbenzoic acid[60]

The proposed reaction mechanism involves attack by DCl on the ring *ortho*-position in the rate-limiting stage of the process (see Scheme 2). Data on the kinetics of the reaction of benzylmercury chloride and its methyl derivatives with deuterium chloride showed that the introduction of methyl groups in the *ortho*- and *para*-positions accelerates the reaction only slightly while a *meta*-methyl group has a significant influence on the rate. The effect of two *meta*-methyl groups is shown particularly clearly (Table 6).

Table 6. Relative rate constants for the simultaneous deuteriation and demercuration of substituted benzylmercury chlorides.

Ring substituent	K_{rel}	Ring substituent	K_{rel}	Ring substituent	K_{rel}
H	1	*p*-Me	2.11	2.6-Me_2	0.36
o-Me	2.44	*m*-Me	24.40	3.5-Me_2	$2.5 \cdot 10^3$

It is noteworthy that the results of such studies fail to reflect sufficiently clearly the effect of ring substituents on the dual reactivity of arylmethylmetal compounds, which is most probably due to incomplete isolation of all the reaction products[63–65].

2. The Nature of the Metal and Solvent

As already stated above, the mode of the reactions of arylmethylmetal compounds is influenced decisively by the hybridisation of the α-carbon atom. Delocalisation of the C – M bond electrons and hence rehybridisation of the

α-methylene carbon atom should depend on the nature of the metal. In the series of organometallic derivatives of magnesium, mercury, lithium, potassium, and caesium, an increase of the polarity of the C–M bond leads to a more intense conjugation of its σ electrons and the π-electron system of the ring. This change has been clearly demonstrated in a study[66] where the absorption spectra of various arylmethylmetal compounds were obtained (Table 7).

Table 7. Dependence of the absorption maximum of the benzyl compounds $C_6H_5CH_2X$ on the nature of the metal.

Substituent	λ_{max}	Substituent	λ_{max}	Substituent	λ_{max}
H	207	MgCl	266	Na	355
HgCl	245	Li	330	Cs	356

The shift of the absorption maximum of the principal band of the benzene chromophore when the substituent is altered arises from the change in the hybridisation of the α-carbon atom. When X = H, the methylene atom is in the state of sp^3-hybridisation — there is then minimal overlapping of the hybrid orbital with the π-electron system of the ring. The observed bathochromic shift of the absorption maximum in the spectra of organometallic compounds is associated with an increase of the overlapping of the valence electron orbital with the π-electron system of the aromatic ring. The increase is related to the change in the hybridisation of the α-carbon atom, the orbital of the valence electrons assuming an increasing p-character with increase of the amount of ionic character of the C – M bond. The maximum bathochromic shift in the case of ionic structures of sodium and caesium derivatives corresponds to the sp^2-hybridisation of the α-carbon atom. An analogous bathochromic shift with increasing electropositive properties of the metal has been observed in the absorption spectra of diphenylmethyl, triphenylmethyl, and fluorenyl anions[67, 68].

The change in the hybridisation of the methylene carbon atom as a function of the nature of the metal entails a change in its nucleophilicity and affects the reactivity of the organometallic compound as a whole. The closer the state of the α-carbon atom to sp^3-hybridisation the smaller the amount of ionic character of the C – M bond and the greater the degree of shielding of the α-carbon atom by the metal atom. This hinders the attack on the central carbon atom by the electrophilic agent and consequently leads to an increase of the relative reactivity of the aromatic carbon atoms. Conversely, when the α-carbon atom is sp^2-hybridised (maximum ionic character of the C – M bond), the central carbon atom is most accessible to interaction with the electrophilic agent. Despite the more marked conjugation of the C – M bond electrons with the aromatic ring π-electron system, in this case the aromatic carbon atoms are not as a rule attacked. Consequently dual reactivity should be shown to the greatest extent by derivatives of the most electronegative metals, for example Group III metals, and to the smallest extent by alkali metals.

Unfortunately a systematic comparison of the reactivities of arylmethyl derivatives of various metals has not been made under identical conditions, particularly due to the differences in the methods used to prepare the arylmethyl derivatives of different metals and their different solubilities. However, it is known that in the reactions of α-chloromethyl ether[36], dipropyl sulphate[37], and dicyanogen[57] carried out under comparable conditions with benzylmagnesium chloride and benzyl-lithium, dual reactivity is observed only for the magnesium derivative. The hypothesis of an appreciable dual reactivity of Group III metals has been confirmed by studies on tribenzylaluminium[69, 70] and tribenzylboron[11–13] published in recent years.

Together with these qualitative observations, individual quantitative data, listed in Table 8, have been published recently.

Table 8. Effect of the metal on the dual reactivity.

Nucleophilic agent	Electrophilic agent	Metal (electronegativity)	Ratio of yields of ring-substituted products and α-carbon addition products	References
$[Ph_2C{-}NPh]^{2-}2M^+$	iso-PrCl	K(0.91) Na(1.01) Li(0.97)	0.02 0.6 1.2	71, 72, 73
	iso-PrBr	K Na Li	0.1 1.0 3.0	71, 72
$\left[\begin{matrix}PhC{-}O\\ \vert\\ C_6H_{11}\end{matrix}\right]^{2-}2M^+$	CO_2	Na Li	1.7 2.4	74
$PhCH_2M$	$MeCH_2CHO$	Li $Mg_{1/2}$(1.23) $Al_{1/3}$(1.4)	0 0.4 5.0	75

The effect of the solvent on the reactivity of organometallic compounds is related primarily to the solvation of the cation and the state of the ion pairs in solution. The use of a polar (and particularly dipolar) solvent, which solvates effectively the metal cation, leads to an increase of the ionisation of the C – M bond, i.e. to an increase of the carbanionic properties of the compound. In other words, the solvent can influence the state of hybridisation of the α-carbon atom in the arylmethylmetal compound. This is confirmed by data for the dependence of the ^{13}C chemical shift in the NMR spectrum of $C_6H_5{}^{13}CH_2Li$ on the solvent (Table 9). (As already stated, the chemical shift reflects directly the state of hybridisation of the carbon atom.)

The data in Table[9] show that, with decrease of solvent polarity, the sp^3 character of the methylene carbon atom in benzyl-lithium increases.

The change in the state of hybridisation of the α-carbon atom naturally has an effect on the conjugation of the valence electrons of the C – M bond with the π-electron system of the ring. This is reflected in the absorption spectra of the organometallic compounds. Thus the main maximum in the absorption spectrum of 1, 1-diphenylhexyllithium undergoes a hypsochromic shift as the polarity of the solvent diminishes[76] (Table 10).

It is evident that the change in the state of hybridisation of the α-methylene carbon atom due to the change in the solvent or in the metal will have the same influence on

the reactivity of the compound as a whole. In a non-solvating (or in a weakly solvating) solvent, the state of the α-carbon atom approaches sp^3-hybridisation to the maximum extent, which hinders the reaction at this centre of the ambident anion. On the other hand, the use of a solvating solvent should promote the reaction at the α-carbon atom. The data in Table 11 show that a change in solvent polarity has a consistent influence on the proportions of the reaction products. It is important to emphasise that this relation has been found to hold for various reactions — alkylation, addition to the carbonyl group, and deuteriation. It is also significant that results in satisfactory agreement have been obtained for the same reaction by different workers. Admittedly, an unambiguous effect of the solvent is not observed in all cases.

Table 9. Effect of the solvent* on the ^{13}C chemical shift in benzyl-lithium[47, 48].

Solvent	$\delta^{13}C$	Solvent	$\delta^{13}C$
THF	163	Toluene	172
Ether	168.5	Benzene	174.5

* The following abbreviations are used in this and subsequent tables: THF = tetrahydrofuran; DME = 1,2-dimethoxyethane; TMED = tetramethylethylenediamine; HMP = hexamethylphosphoramide; DMF = dimethylformamide.

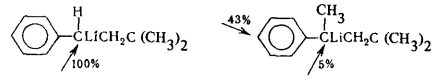
Table 10. Effect of the solvent on the absorption maximum of 1,1-diphenylhexyl-lithium.

Solvent	Dielectric constant	λ_{max}	Solvent	Dielectric constant	λ_{max}
THF	7.58	496	Propyl ether	3.88	422
DME	5.50	495	Benzene	2.28	426
Ethyl ether	4.33	438	Hexane	1.89	415

For example, the results obtained in the deuteriation of α-cumenylpotassium have not been explained, although replacement of ethyl ether by other solvents leads to the disappearance of dual reactivity regardless of solvent polarity. One must also point out the somewhat arbitrary nature of the table column labelled "solvent" — in many cases an excess of the given solvent was added to a solution of the organometallic compound in ethyl ether, so that the reaction actually took place in a mixture of the latter and the added solvent. This should not have an effect when a polar solvent, which effectively solvates the cation, is added, but becomes very significant following the addition of a solvent of low polarity. However, even with this stipulation, the principal feature, namely that a solvent solvating the cation facilitates the reaction with the α-carbon atom while a non-solvating solvent has the opposite effect, is evident.

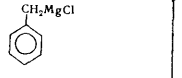
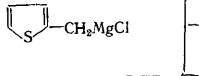
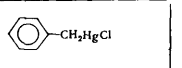
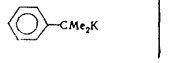
3. Steric Factors

Only isolated data have been published on the effect of steric factors on the dual reactivity of arylmethylmetal compounds. Thus the difference between the reactions of chlorodimethylsilane with the organolithium compounds (XX) and (XXI) has been explained by steric factors[79].



(XX) (XXI)

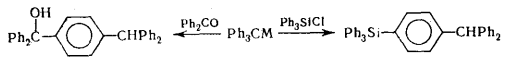
Table 11. Effect of the solvent on the dual reactivity.

Nucleophilic agent	Electrophilic agent	Solvent	Ratio of yields of ring-substitutes products and α-carbon addition products	References
	MeCOCl	Ether DME	0.5 0.5	58
	$ClCH_2OMe$	Ether THF	0.6 0.35	36
		Ether DME	0.14 0	37
	MeCHO	Ether THF	7 0.75	35, 75
	MeCHO	Ether DME THF TMED HMP	4 1.3 0.7 0.4 0.2	32
	$MeCH_2CHO$	Ether THF	0.3 0	75
	t-BuBr	n-Heptane Benzene Ether THF DME	3 2.7 0.07 0.01 0.01	77
	MeCOCl	Ether DME	19 0.9	58
	$CH_2—CH_2$ (O)	Ether DME	8 0	58
	DCl	Dioxan DME DMF	0.5 0.5 0.1	78
	DCl	Pentane Ether DME	0 0.3 0	3

Dual reactivity is shown by the organometallic compound (XXI), in which the carbon atom linked to the metal is tertiary. Similarly a change in reactivity is observed on passing from diphenylmethyl to triphenylmethyl derivatives of alkali metals. The reaction with ethyl benzoate[80], benzaldehyde, and benzophenone[81] results primarily in the formation of products of addition to the α-carbon atom, the secondary process yielding considerable amounts of products of *para*-substitution in the aromatic ring[82–84].

As already stated, derivatives of heavy alkali metals do not as a rule exhibit dual reactivity owing to their carbanionic properties. However, when cumenylpotassium is deuteriated[3], products resulting from attack on the ring are formed, which can probably be accounted for by steric

hindrance at the α-carbon atom. Steric factors have a particularly marked effect in those cases where both reactants (the nucleophilic and electrophilic agents) are sterically hindered. The interactions of alkali metal triphenylmethides with benzophenone[83] or chlorotriphenylsilane[4] can serve as examples:



The problem of the relation between the electronic and steric factors in reactions of dianions having the formula $Ar_2\bar{C}-\bar{X}$, where X = O or NC_6H_5, is somewhat more complicated. The presence of the second nucleophilic centre sharply increases the reactivity of the carbanion. Thus, in contrast to alkali metal diphenylmethides (XXII), which do not react with t-butyl chloride and acid nitriles in liquid ammonia[85,86], the dimetal derivatives of benzophenone (XXIII) interact with the above compounds under the same conditions[86,87]. The alkylation reaction proceeds not only with the α-carbon atom but also with ring carbon atoms. In the alkylation of these two compounds and also of compound (XXIV) with isopropyl bromide, the reaction proceeds in all cases, but compound (XXII) is alkylated only at the α-carbon atom, while (XXIII) and (XXIV) exhibit dual reactivity. The latter is probably due to the joint effect of both the electronic and steric factors:

$Ph_2CH^-M^+$ (XXII) $[Ph_2C-O]^{2-}2M^+$ (XXIII) $[Ph_2C-NPh]^{2-}2M^+$ (XXIV)

The study of the dual reactivity of the dianions $Ar_2\bar{C}-\bar{X}$ is complicated by two factors. Firstly, reactions involving the second anionic centre, for example *O*- or *N*-alkylation, are possible in addition to the dual mode of reaction of the ambident arylmethyl system. A reaction of the former type is observed in methylation but does not occur when more complex alkyls are employed[72,88]. Secondly, ring-substituted products can be formed not only as a result of electrophilic attack on the carbanion but also as a result of reactions by the intermediate radical-anion $Ar_2\dot{C}-X$. The formation of such radical-anions as a result of one-electron transfer in reactions of dianions has been postulated by a number of workers[72,89,90]. Radical-anions of the arylmethyl type are known to have a marked capacity for reactions involving ring carbon atoms (see, for example, Schenck and Matthias[91] and Holme and Crossland[92]).

4. Electronic Structure of the Electrophilic Agent

According to a familar rule, an increase of the positive charge on the electrophilic centre and also an increase of the polarity of the electrophilic agent should increase the tendency towards the reaction involving the atom of the ambident system which has the highest electron density. The numerous pieces of evidence supporting this hypothesis in relation to a series of ambident anions have been obtained as a rule in the alkylation reaction. In relation to arylmethyl anions, the reaction has been little studied, although there are isolated examples of a qualitative confirmation of the above rule in the case of alkylation[37]. The addition of the arylmethyl anion to the C = O bond (reactions with aldehydes, ketones, and acid derivatives) is more typical and better investigated. The electrophilic properties of carbon in these compounds increase in the series $CONR_2 < COOH < COOR < COR < COH < COCl$. The capacity of the reactants to form benzene ring-substituted products increases in the same sequence.

On the other hand, similar reactions have not been described for acids and amides, a few isolated observations have been made for esters, and aldehydes and acid chlorides are typical "anomalous" reactants. In a series of compounds of the same class, a change in the charge of the carbon atom due to the change in the properties of the aliphatic chain has a marked influence on the mode of reaction. Thus, whereas the reaction of benzylmagnesium chloride with acetonitrile results in the formation of the α-addition product only, the reaction with trifluoroacetonitrile yields up to 40% of the *ortho*-substituted products[7,8]. It has been shown[30,75] that in reactions of benzylmagnesium chloride with aldehydes, 100% substitution of the aromatic ring is observed only for formaldehyde, the yield of the ring-substituted product decreasing with increase in the length of the aliphatic chain. Branching at the α-atom, which reduces the charge of the carbonyl carbon atom§ has a particularly marked effect. On the other hand, when reactions of benzylmagnesium chloride with trifluoroacetaldehyde and acetaldehyde are compared, it is found that the ratio of the reaction product yields involving the ring and the α-carbon atom is greater by a factor of ten in the first reaction than in the second[35].

Table 12. Effect of reactant ratio on the yield of reaction products.

Nucleophilic agent	Electrophilic agent	Order of addition* and reactant ratio	Yield, %			References
			α-	*ortho*-	*para*-	
$PhCH_2MgCl$	PhCHO	Forward 1 : 1	90—84	0—2	—	84
		Reverse 1 : 1	43—40	20—60	—	93
$PhCH_2MgCl$	$ClCH_2OMe$	Forward 1 : 1	43	17	10	37
		Reverse 1 : 1	36	9	11	
$PhCH_2MgCl$	MeCHO	Forward 3 : 1	22	38 **	—	35
		Reverse 1 : 1	11—8	76—88 **	—	
α-$C_4H_4SCH_2MgCl$	$(CH_2)_2O$	Forward 1 : 1	45	53	2	58
		Reverse 1 : 1	25	72	3	
$[Ph_2C-NPh]^{2-}2Li^+$	iso-PrCl	Forward 1 : 1	46	45	9	72
		Reverse 1 : 2	34	57	9	

* The forward order of addition is understood as the addition of the electrophilic agent to the nucleophilic agent.
** The overall yield of the *ortho*-substituted product and the product of the simultaneous substitution in the *ortho*-position and at the α-carbon atom

An unusual example is provided by the deuteriation of cumenylpotassium[3]. Deuteriation of the ring, which takes place mainly in the *para*-position, depends on the polarity of the deuteriating agent. Whereas interaction with heavy water leads to selective α-deuteriation ($K_\alpha/K_{ring} > 500$), the ratio is 65 and 4.5 respectively in the reactions of CH_3COOD and with DCl.

There are also quite definite literature data concerning the effect of the ratio of the electrophilic and nucleophilic agents on the dual reactivity. Scheme 1 shows that the presence of an excess of the organometallic compound should favour the formation of products of the reaction

§ In this case, one cannot rule out also the effect of steric factors, as pointed out by Sadaaki and Yuya [spelling of names uncertain (Ed. of Translation)][75].

involving the α-carbon atom, while an excess of the electrophilic agent should promote ring substitution. This has been confirmed by experimental data (Table 12). It is interesting to note that the yield of *para*-substituted products is almost independent of the ratio of the reactants.

A brief examination of the mechanism of the "anomalous" reactions of arylmethyl compounds and the factors influencing these reactions leads to the conclusion that we now know the main general characteristics of this process. Moreover, in certain cases it is possible to alter the mode of reaction in order to obtain the desired result. However, our knowledge of the reactions of arylmethylmetal compounds requires further expansion. The question of the *para*-substituted products is least clear — even simple accumulation of experimental data on this problem is of definite interest and can lead to a hypothesis concerning the mechanism of *para*-substitution. On the other hand, the determination of the mechanism will ultimately make it possible to treat the arylmethyl anion not as an ambident species, which was done in the present review as a necessary simplification, but as a polydent anion, and to find conditions for reactions by such systems which are selective with respect to α-carbon atoms and the *ortho*- and *para*-carbon atoms in the ring.

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