Translated from *Uspekhi Khimii*, 45, 661-694 (1976) U. D. C. 547.1'13 : 547.22

The Interaction of Organometallic Derivatives with Organic Halides

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The possible mechanisms of the reactions of organometallic derivatives with organic halides, including the metal-halogen and recombination (Wurtz) reactions, are examined. Particular attention is devoted to the analysis of the composition of the products and the stereochemistry of the reactions and to the results obtained using physicochemical methods. The bibliography includes 156 references.

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I. INTRODUCTION

The interaction of organometallic compounds RM with alkyl halides R'X is a complex process which may proceed as an exchange reaction (known for sodium, lithium, magnesium, and barium derivatives):

$$RM + R'X \rightarrow RX + R'M,$$

or as a recombination reaction (the well known Wurtz reaction involving RLi or RNa):

$$RM + R'X \rightarrow R{-}R',$$

accompanied by the formation of RR, R'R', RH, R'H, R(-H), and R'(-H). The problem of its mechanism is still controversial and the possibility of heterolytic and radical pathways is being discussed.

A tendency has arisen in recent years to consider many reactions previously classified as nucleophilic or electrophilic substitution processes in terms of oxidation–reduction interactions. Within the framework of this concept, the interaction of a donor (nucleophile) and acceptor (electrophile) takes place as a result of electron transfer (*single electron transfer*, SET mechanism) and leads to the formation of radicals or radical-ions. There is no doubt that the objective cause of the development of this concept (and the reason why it has proved attractive) has been the appearance of physicochemical methods whereby one can detect the formation of radical-ion and radical species directly or indirectly the latter method includes chemically induced dynamic nuclear polarisation (CIDNP).

Naturally the attention of the supporters of this concept has been attracted primarily by organometallic compounds which can behave, by virtue of their high capacity for oxidation, as electron donors in relation to many organic and inorganic acceptors. The first attempts to consider certain reactions of organometallic derivatives with carbonyl compounds and alkyl halides from the standpoint of a radical mechanism were made as early as the beginning of this century on the basis of the composition of the observed products or the appearance of a colour in the reaction mixture, although the formation of "anomalous" products in many instances could be accounted for also within the framework of a heterolytic mechanism. However, the possibility of the simultaneous occurrence of reactions via several pathways was hardly ever considered, although the question of the possible change from an ionic to a radical mechanism frequently arose when the nature of the metal atom, the structure of the reactants, and the reaction conditions (primarily temperature and the solvent) were altered.

Attempts are now being made to unify the two mechanisms within the framework of the concept of single electron transfer (SET), as a result of which there is radical recombination with formation of RR' (the classical Wurtz reaction) and the formation of products arising from the radicals R· and R'· liberated from the cage can occur.

From the standpoint of the SET mechanism, the general scheme for reactions of RM with R'X can be represented as follows:

$$RM + R'X \rightleftarrows \begin{bmatrix} R^{\cdot} & X^{-} \\ R^{\cdot} & M^{+} \end{bmatrix} \xrightarrow{a} R{-}R' \quad \xrightarrow{b} R'M + RX \quad \xrightarrow{c} R'^{\cdot} + R^{\cdot}$$

In this review we attempted to analyse all the mechanisms of both exchange and Wurtz reactions which are being discussed in the literature, without trying to cover the entire available data and all the synthetic aspects of these reactions. It was found that the simple SET mechanism cannot explain all the observed characteristics of the reaction between R'X and RM. This applies particularly to stereochemical data, since reactions of organometallic compounds with optically active halides, which lead not only to racemisation but also to inversion (in the Wurtz sense) and to racemisation with partial or complete retention of configuration (in the metal-halogen exchange reactions), are known.

II. REACTIONS WITH ORGANOMAGNESIUM COMPOUNDS

The first systematic study of the reactions of organomagnesium compounds with alkyl halides was apparently undertaken in 1913 by Späth[1], who proposed a radical mechanism, in contrast to Abegg's ionic mechanism[2]. In many cases the main reaction products were the hydrocarbons R_2, R'_2, R(−H), RH, etc., which had been previously regarded as side products, and not the mixed hydrocarbon RR′ (the product of the Wurtz reaction). It is interesting to note that the hydrocarbon RR′ was formed in a high yield when halogeno-derivatives of the allyl and benzyl types or derivatives with a tertiary group R were introduced into the reaction[1-4]. As will be shown below, the same effect is observed also in the corresponding reactions of organosodium and organolithium derivatives with yields of the hydrocarbon RR′ reaching 70–98%.[5-9] It is difficult to account for these results from the standpoint of a radical mechanism, since the extent of the liberation of the radicals from the cage should increase with increase of their stability. Indeed, when R = Ph_3C, a large amount of triphenylmethyl radicals of triphenylmethyl peroxide is always formed in the reaction[10-14]. For example, the yield of tetraphenylmethane in the reaction of Ph_3CCl with PhMgBr has been usually 0.5–5%[10] and the yield increased to 12% only under specially selected conditions (temperature, solvent, order of addition of reactants)†. The replacement of phenylmagnesium bromide by the corresponding iodide led to the formation of the triphenylmethyl radical and biphenyl alone (not even traces of Ph_4C were detected).[11] The yield of tetraphenylmethane in the reaction of PhMgBr with triphenylmethyl ethers Ph_3COR (R = Me, Et, or Ph) reached 10–12% for the first two groups and was more than 20% in the reaction with phenyl ether at 150°C. The last reaction occurred most readily, but the reduction of temperatures to about 35°C led to the formation of triphenylmethyl peroxide alone[10]. However, one should note that exceptionally high yields of Wurtz reaction products are formed even with triphenylmethyl halides when benzyl (or methyl) Grignard reagents are introduced into the reaction[1,2,15,16].

In certain early studies, the formation of R'_2 alone was observed when RMgX was allowed to react with R′X. Thus according to Schmidlin and Massini[17], the only product found in the reaction of phenylmagnesium bromide with β-chloromethylnaphthalene was symmetrical di-(β-naphthyl)ethane. A similar result was obtained by Fuson[18], who isolated the corresponding bibenzyl $(o\text{-}CNC_6H_4CH_2)_2$ after the reaction of methylmagnesium bromide with o-cyanobenzyl bromide. On this basis, he suggested that the Grignard reagent promotes the radical reaction of R′X.

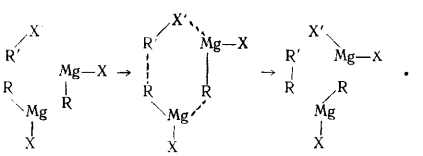
All the early studies suffered from one disadvantage—the lack of a complete analysis of the products and in the first place from the loss of volatile hydrocarbons. The first disadvantage was apparently overcome by Fuson[19], who analysed in detail the products of the reaction of MeMgI with benzyl halides (Hal = Cl, Br, or I) and showed that, apart from ethylbenzene and bibenzyl, which had been detected also by other investigators[1,4], ethane is formed in the reactions in equimolecular amounts with respect to bibenzyl. We may note that the yield of ethylbenzene decreased appreciably in the sequence $PhCH_2Cl > PhCH_2Br > PhCH_2I$ (by a factor of about 2.5 on passing from the chloride to the iodide); the amounts of ethane and bibenzyl increased under these conditions, albeit only slightly (to an extent of about 20%). These results can be accounted for from the standpoint of both the SET mechanism, i.e. by a change in the ease of rupture of the C–Hal bond in the above sequence and by the occurrence of two consecutive reactions—exchange and Wurtz reactions, since the possibility of the exchange processes also increases on passing from the chloride to the iodide. However, the author himself believed that the exchange reaction has no bearing on the formation of ethane, since he had shown for benzyl chloride that methyl chloride is absent from the reaction products:

$$PhCH_2Cl + CH_3MgI \rightarrow CH_3Cl + PhCH_2MgI,$$

and furthermore in the reaction of methyl iodide with CH_3MgI ethane is formed in a yield of only 21%:

$$CH_3I + CH_3MgI \rightarrow CH_3CH_3.$$

The possibility of a radical mechanism was considered by Gilman and Kirby[20], who observed that the reaction of diphenylmethylmagnesium bromide with dimethyl sulphate leads to the almost quantitative formation of tetraphenylethane. However, in their book dealing with organomagnesium compounds[21], Kharash and Reinmuth noted the possibility of a radical mechanism of the Wurtz reaction and expressed the view that this pathway probably occurs only rarely on the grounds that there is no statistical distribution of hydrocarbons in the reaction products (RR′, R_2, and R'_2) or the corresponding disproportionation products [RH, R(−H), R′H, and R′(−H)]. We may note that, from the standpoint of the SET mechanism, this argument appears unconvincing, since the ratio of the yield of recombination products and the extent of the liberation of radicals from the cage can vary within wide limits, depending on the stability of the radicals and the reaction conditions. As a second argument, Kharash and Reinmuth quote the fact that in real radical processes, which were believed to be the reactions of R′X and RMgX in the presence of transition metal salts, quite different products are formed. Finally, the main argument was the fairly high yields of the hydrocarbons RR′ observed for R = $PhCH_2$, $CH_2 = CH - CH_2$, CH_3OCH_2, etc., i.e. in those reactions where fairly stable radicals should have been formed‡. Kharash suggested that there is no unique mechanism explaining all the observed instances of the reactions; he believed that the trimolecular "push-pull" mechanism is most common:



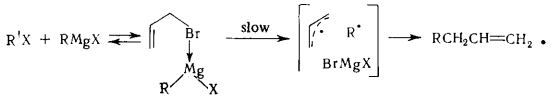
† Gilman and Jones[15] observed the formation of 47.7% of p-biphenylyldiphenylmethane (not detected by other workers), which undoubtedly confirms the presence of Ph· in the system.

‡ We may note that the absence of a β-hydrogen atom is a characteristic feature of all the groups enumerated as well as CH_3.

The view that, depending on the structure of the reactants and the conditions in the reaction, the mechanism of the latter may change, was questioned by Gough and Dixon[22], who investigated the kinetics of the reaction of allyl bromide with a series of organomagnesium compounds. In terms of their reactivity, the derivatives RMgX were arranged in the following sequence:

RMgX	PhMgBr	n-BuMgCl	s-BuMgCl	t-BuMgCl
$K_{rel,\ 25°}$	1	2.71	22.6	107

According to the authors, the observed sequence in which the reactivity varies and the applicability of the Taft equation with $\rho = -1.9$, the formation of 2,2,3,3-tetramethylbutane in the reaction with t-BuMgCl, and the ESR signal observed in the reaction with n-BuMgCl (although the yield of n-$BuCH_2$–CH=CH_2 was 90%) indicate the SET mechanism:



The conclusion that the reaction of phenylmagnesium iodide with iodobenzene has a radical mechanism was based on the detection of the label in the reaction product when deuterobenzene was used as a solvent (in admixture with ether).[23]

The composition of the products formed in the reactions of phenylmagnesium bromide and benzylmagnesium bromide with a series of arylalkyl chlorides is regarded[24] as proof of the SET mechanism, since, according to Gilman's data[15], exchange processes do not occur in these systems.

		Yield, %			
R'X	RMgX	RR'	R'R'	RR	RH
$PhCH_2Cl$	PhMgBr	56	6	4	12
$(Ph)_2CHCl$	»	60	6	6	10
Ph_3CCl	»	46	5	4	10
Ph_3CCl	$PhCH_2MgCl$	55	5	15	—

The observed reactivity series $Ph_3CCl > Ph_2CHCl > PhCH_2Cl$, $PhCH_2MgX > PhMgX$, which is the same as the series based on the increasing stability of the groups R and R', is also consistent with the radical reaction mechanism. A similar mechanism has also been proposed[156] for the reaction of phenylmagnesium bromide with bromotriphenylmethane on the basis of the analysis of the composition of the products. When the reaction was carried out in ethyl ether, triphenylmethanol, triphenylmethane, biphenyl, ethylbenzene, and α-phenylethyl alcohol were detected in the reaction mixture, while in the presence of oxygen triphenylmethyl peroxide was found.

Finally, data confirming that alkyl radicals are formed even in the reactions of alkylmagnesium halides with "simple" alkyl halides have been obtained in recent years. This is indicated by data based on the CIDNP of the reaction products. Thus Ward et al.[25] observed CIDNP in the products of the reaction of t-butyl bromide with t-butylmagnesium chloride and of n-butyl iodide with n-butylmagnesium chloride in tetrahydrofuran (THF). The former reaction leads to the formation of isobutene (6%), isobutane (39%), and tetramethylbutane (6%), the vinyl protons of isobutene and but-1-ene and the methyl protons of isobutane being polarised, which suggests the formation of t-butyl and n-butyl radicals§.

CIDNP was likewise observed in the products of the reaction of diethylmagnesium with ethyl iodide and isopropyl iodide in THF.[26] The disproportionation products of the groups R and R' were mainly formed (ethane, ethylene, propane, and propene) with only a small amount of recombination products. The initial iodides were also polarised, which is associated, according to the authors, with a relay transfer of the radical in the chain process:

$$R'I + R^{\cdot} \rightarrow R'^{\cdot} + RI.$$

The authors believe that exchange processes can be hardly responsible for the observed polarisation of the halide, since in the reactions of iso-PrI with Et_2Mg the exchange process would have led to the formation of appreciable amounts of ethyl iodide, which was not observed under the conditions of the NMR experiment. However, the reaction of diethylmagnesium with iodobenzene occurred mainly as an exchange process:

$$\underset{}{Et_2Mg} + \underset{}{PhI} \rightarrow \underset{72\%}{Ph_2Mg} + \underset{92\%}{EtI} + \underset{5\%}{PhH} + \underset{5\%}{PhEt},$$

The yield of ethylbenzene increased with time owing to the condensation of Ph_2Mg with EtI.

Ideas concerning the mechanism, including SET, of reactions involving ArHal (the Wurtz–Fittig reaction) have been put forward[27] on the basis of the detection by ESR of radical-anions in the reaction of phenylmagnesium bromide and phenyl-lithium with nitrosated halogenobenzenes.

When the results of the reactions are considered from the standpoint of the SET mechanism, then evidently the ratio of the radical recombination products and products arising as a result of the liberation of radicals from the cage should depend on the structure of the radical and also on the stabilities of the individual components of the radical-ion pair. For example, the reaction of 1-adamantyl bromide with a series of organomagnesium compounds RMgX can be analysed from this standpoint[28]. For R = Me, the Wurtz reaction was achieved with an 83% yield, but the latter fell sharply for R = $PhCH_2$ and became zero for R = t-Bu, where adamantane was formed in 84% yield. However, there exists an alternative explanation, which Osawa et al. in fact believe to be valid[28], namely that the reaction mechanism changes when the group R in RMgX alters.

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§ The recently published study by Ward and coworkers[155] suggests that even a small admixture of transition metals present in magnesium can alter significantly the nature of the reaction of RMgX with R'X and can stimulate the development of a radical reaction pathway. The authors showed that the rate of reaction of iso-PrMgBr with iso-PrBr, leading to propane and propene, increases sharply following the addition of bromine, the effect being more marked when less pure magnesium (99.9 instead of 99.998%) is used; a considerable polarisation of the reaction products was observed at the same time. It is suggested that the process is catalysed by an oxidised form of the metal, for example the metal oxidised by the halogen present in R'X. We may note that in this version we are dealing with a Kharash reaction and not a Wurtz reaction. However, it is still not clear to what extent such admixtures can distort the results discussed above.

It is interesting that monobromonorcarane was obtained in high yield in the reaction of 7,7-dibromonorcarane with methylmagnesium bromide in THF,[29] which makes it possible to employ RMgX in such systems as a reducing agent for preparative purposes.

It is appropriate to mention here the reaction of organomagnesium compounds RMgBr (R = Ph, $PhCH_2$, or n-Bu) with (trichloromethyl)carbinyltoluene-*p*-sulphonates $R'-CHCCl_3$ (R' = Alk or Ar) in ether, for which a free
|
OTos
radical mechanism has been proposed[30]. The reaction results in a mixture of products, the composition of which in each specific case depends on the nature of RMgBr and the toluene-*p*-sulphonate derivative. For example, when R = R' = Ph, the products are ββ'-dichlorostyrene (78%), benzene (64%), styrene (42%), and ethyl α-phenylethyl ether (13%). In the presence of benzylmagnesium bromide, the corresponding ether was not detected, but bibenzyl was formed in a quantitative yield. The authors believe that the first reaction stage involves electron transfer:

$$RMgBr + \underset{\underset{OTos}{|}}{R'CHCCl_3} \rightarrow R^{\cdot} + \underset{\underset{OTos}{|}}{R'\dot{C}Cl_2} + MgBrCl + TosMgCl.$$

All the products detected have been accounted for by further reactions of the above radicals (including their reactions with ether). The formation in the initial reaction step of the radical $R'CHCCl_3$ appears to be no less likely and its further reactions (together with those of R·) should naturally lead to the same composition of the products.

A mechanism including a reaction transfer stage has also been proposed for the reaction of phenylmagnesium bromide with triphenylmethyl acetate in ether, which proceeds in an unusual manner[31]. The use of acetate labelled with ^{18}O shows that the entire label passes to acetic acid:

$$CH_3-\overset{\overset{^{18}O}{\parallel}}{C}-{}^{18}OCPh_3 + PhMgBr \rightarrow \underset{60\%}{(Ph_3CO)_2} + \underset{80\%}{CH_3C(=^{18}O)-{}^{18}OH},$$

i.e. the reaction takes place with dissociation of the O–CPh_3 bond. Apart from trityl peroxide and acetic acid, acetophenone (14%), benzophenone (12%), triphenylmethane (23%), biphenyl (23%), and triphenylmethanol (about 5%) were detected in the reaction products.

III. REACTIONS WITH ORGANOSODIUM AND ORGANOLITHIUM COMPOUNDS

Ideas concerning the mechanism of the classical Wurtz reaction between RNa or RLi and R'X have undergone approximately the same development. In 1927 Marvell et al.,[32] who investigated the reaction of butyl-lithium with a wide variety of halogeno-derivatives, showed that the yield of RR' varies within very wide limits as a function of the nature of R'X. In many cases hydrocarbons of the type R'R' were isolated together with RR'. Thus *trans*, *trans*-1,4-diphenylbuta-1,3-diene was obtained together with 1-phenylhex-1-ene in the reaction involving α-bromostyrene. The authors showed that it is formed from the radical $PhCH=CH_2^{\cdot}$ and not as a result of exchange and subsequent recombination processes. This conclusion is based on the fact that the reaction with almost all the R'X was accompanied by the appearance of a colour (particularly pronounced for α-bromostyrene and chlorotriphenylmethane), which disappeared at the end of the reaction. The reaction of Ph_3CCl led to the formation of triphenylmethyl peroxide together with 1,1,1-triphenylpentane. An unexpected result, which is difficult to account for by differences in the structures of the R'X, was obtained in the reaction of butyl-lithium with isomeric bromotoluenes. For *p*-$BrC_6H_4CH_3$, the product of the Wurtz reaction was obtained in 76% yield, while the *m*- and *o*-isomers give almost quantitative yields of toluene.

We may note that, in the early studies on the Wurtz reaction as well as in the studies published much later than the investigation described above, the formation of products of the disproportionation of RH, R'H, R(−H), R'(−H), and (or) the symmetrical hydrocarbons R'_2 and R_2 was frequently observed together with that of the recombination product RR', but the possibility of a radical mechanism was either not discussed or was frequently ruled out on *a priori* grounds. For example, Morton et al.[33] stated that all the recombination and disproportionation products in the reactions of R'X with RNa can be explained without resorting to the hypothesis of the existence of radicals (although they did not rule out completely the possibility of a free radical pathway). Incidentally the conclusion that the hydrocarbons RH and R(−H) are not formed as a result of the disproportionation of radicals was based on the finding that in the reactions investigated the yield of RH as a rule greatly exceeded the yield of R(−H). Many other investigators also hold the view that the Wurtz reaction has an ionic mechanism (see, for example, Refs. 7 and 34–38). The stereochemical data discussed below constitute an important argument in this connection.

Defending the ionic reaction mechanism, Eastham and Gibson[39], wrote that the formation of the alkane RH and the alkene R(−H) does not by itself demonstrate the existence of the radical R·, i.e. it is the result of the hydride reduction of R'X by the β-hydrogen atom of the RM molecule and not of the disproportionation of the radical. In the reaction of butyl-lithium with 2-bromo-octane in hexane, which they investigated, octane (66%) and dodecane (32%) are formed, while in the reaction with bromocyclohexane the products are cyclohexane (56%), butylcyclohexane (32%), and cyclohexene (5%). Under these conditions, other halogeno-derivatives—1- and 2-chloro-octanes, 1-chloroisopentane, 4-chloroheptane, and fluoro- and chloro-cyclohexanes—were also reduced to alkanes. Using butyl-lithium labelled with tritium in the β-position, the authors obtained tritiated cyclohexane, which enabled them to suggest a mechanism for the reduction of halogeno-derivatives by the β-hydride atom of butyl-lithium:

$$BuLi + R'X \rightarrow \text{[cyclic transition state: } R-CH_2-CH(CH_2CH_3)-CH_2-H \cdots Li \cdots X\text{]} \rightarrow RCH_3 + LiX + CH_3CH_2CH=CH_2 .$$

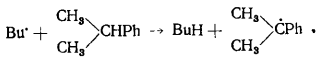
However, from our point of view, the hydride shift can also occur as a multistage process including an electron transfer stage:

$$\text{>C(H)–C:M} + R'X \rightleftharpoons \left[\text{>C(H)–C}^{+}\text{ M}^{+}\ \ R'^{\cdot}\ X^{-}\right] \rightarrow \text{olefin} + R'H + MX .$$

This conclusion was based on the observation of the CIDNP of the methine proton of triphenylmethane in the reaction of Ph_3CX (X = Cl, Br, or ClO_4) with di-n-butyl

or di-s-butyl-mercury and also with triethylsilane. In this case the results do not rule out the SET mechanism, which we believe can be invoked to account for the ease of reduction by metal hydrides of the C–Hal bond involving a bridgehead halogen[41]. We may note that Jefford et al.[41] assume that the reaction takes place as a result of cationoid abstraction of the halogen and the protonation of the resulting carbanion by the solvent.

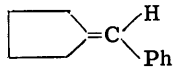
Some evidence for the formation of radicals in the Wurtz reaction was obtained by Bryce-Smith[42]. He used cumene as a trap for the butyl radical formed in the reaction of the butyl derivatives of lithium and sodium with butyl halides:



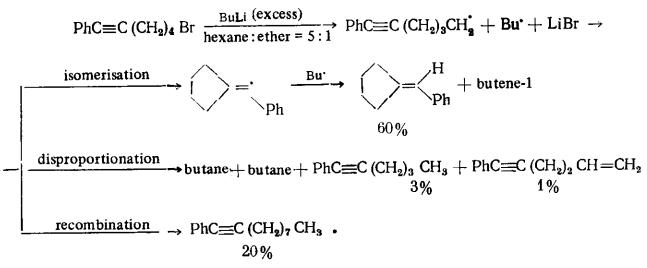
The resulting radical then dimerises to 2,3-dimethyl-2,3-diphenylbutane.

Sauer and Braig[9] also considered electron transfer as the first stage of the Wurtz reaction and showed that the reaction of 2-bromo-octane with allyl-lithium in ethyl ether or TMF (at 0°C) gives an 87–95% yield of the corresponding hydrocarbon RR′ and only trace amounts of octane, octene, and 7,8-dimethyltetradecane. The addition of cumene has no influence on the reaction. However, the interaction of the same bromide with ethyl- or n-propyl-lithium (at 0° or 35°C) leads to the formation of a mixture of the hydrocarbons R′H, R′(–H), RR′, and R′R′ in the proportions (0.6–0.9) : (0.6–0.9) : 1.0 : (0.5–0.6). When cumene is added, about 8% of bicumenyl is formed. According to the authors[9], the products detected are formed via the recombination or disproportionation of the radicals R· and R′· arising in the primary reaction step.

The possibility of a radical mechanism sometimes assumes special interest, for example in the reaction of $PhC{\equiv}C(CH_2)_4Br$ with BuLi, which leads to the cyclisation product[43,44]



Kandil and Dessy[43] suggested that it is formed as a result of the anionic cyclisation of the corresponding organolithium compound $PhC{\equiv}C(CH_2)_4Li$, arising in the exchange reaction. Ward[44] adduces convincing data in support of a radical mechanism of the cyclisation reaction:



Similar results have been obtained with ethyl- and t-butyl-lithium.

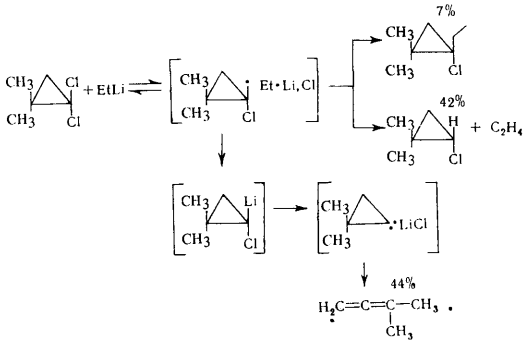
Direct detection of radicals by ESR in the reaction of ethyl-lithium with chlorotriphenylmethane was achieved by Shilov et al.[45] The concentration of triphenylmethyl radicals exceeded the equilibrium value, which undoubtedly indicated an SET mechanism. Ethane and ethylene were formed from methyl radicals; however, the absence of deuterium from ethane when the reaction was carried out in a deuteriated solvent forced the authors to assume that the ethyl radicals do not exist as kinetically independent species and that a complex with EtLi is formed in which disproportionation takes place. Ward[46] believes that there is a relation between the complex formation process and the state of aggregation of the organolithium compounds in solution.

Proof of the formation of radicals in the primary reaction step was obtained for simple alkyl halides by D'yachkovskii and Shilov[47] in a study of the reaction of ethyl-lithium with ethyl iodide, the products of which were ethane, ethylene, and butane, ethylene being formed according to the authors on disproportionation of the radical R· in the cage. The relative yield of ethane decreased when the reaction was carried out in decalin with added anthracene and also in benzene and toluene, which are known to be capable of interacting with alkyl radicals. The relative yield of ethane falls even more when α-methyl-styrene is added to decalin (by a factor of ten compared with the yield of ethane in pure decalin). When experiments in deuteriated solvents were carried out, monodeuteroethane was detected: 2.3% in C_6D_6, 3% in C_6D_{12}, and 5.6% in $C_6D_5CD_3$.

A radical mechanism may also be considered for the exchange reaction between RLi and R′X. The exchange reactions of PhI with RLi, where R = alkyl, cycloalkyl, alkenyl, or aryl, have been used by Applequist and O'Brien[48] to estimate the relative stabilities of various compounds RLi (i.e. the stabilities of the carbanions), and data for the equilibrium positions in the system served as a basis for a method of determining the pK_a values for CH acids[49]. It has been suggested that the reaction is electrophilic. According to Wittig[50], the main argument has been the ease of carrying out this reaction with bromo-derivatives of bicyclic compounds containing bridgehead bromine, for example bromotriptycene, for which S_N2 and S_N1 reactions are hindered or even impossible. According to Wittig, the electrophilic attack is preceded by the nucleophilic attack of R^- on the bromine, which then expands its electron shell to a decet. Other investigators[51] also support the view that the exchange processes are heterolytic. However, the ease of exchange in such systems does not conflict with a radical mechanism, including SET, either.

Evidence for the radical mechanism of the exchange reaction was obtained with the aid of CIDNP studies[52–57]. Thus Ward and Lawler[52] observed the polarisation of protons in the but-1-ene and isobutene formed in the reaction of n-butyl-lithium and t-butyl-lithium with butyl bromide in hexane. The octane formed is probably also polarised, but the observation of the polarisation is hindered by the superposition of the signal due to the solvent and the reactants. In the almost "pure" exchange reaction between ethyl-lithium and iodobenzene[53] the methylene proton of the ethyl iodide formed in 80% yield are polarised. Similar results were obtained in a study of the reaction of ethyl iodide with ethyl-lithium (in benzene at 40°C), where the polarisation of the methyl and methylene protons of the ethyl iodide formed in the course of the exchange was observed[53]. Both iodides (s-BuI and n-BuI) were polarised in the reaction of n-BuLi with n-butyl iodide in consequence of the reversibility of the reaction. A similar situation was observed in the converse exchange reaction—the reaction of s-butyl-lithium with n-butyl iodide[53]—and in the reaction of n-butyl-lithium with n-butyl iodide and isopropyl iodide, where the vinyl protons of propene and but-1-ene were found to be polarised[54]. We may note that the polarisation of the protons in the molecule of the organolithium compound has not been observed in any of the reactions, in agreement with the data of

Shilov et al.,[45] showing the absence of ethyl radicals in the reaction of ethyl-lithium with chlorotriphenylmethane. Positive CIDNP has been observed in the products of the reaction of ethyl-lithium with 1,1-dichloro-2,2-dimethylcyclopropane[58], i.e. in 3-methylbuta-1,2-diene and 1-chloro-2,2-dimethylpropane.



Several instances of the observation of CIDNP in the products (RR′) of the Wurtz reaction proper, for example in the reaction of ethyl-lithium with $\alpha\alpha'$-dichlorotoluene[59], are known. This example is of interest, because it has been used to demonstrate the dependence of the observed polarisation of α-chloro-α-phenylpropane on the applied magnetic field. Polarised ethane was formed in the reaction of ethyl iodide with sodium in dimethoxyethane (DME), which enabled the authors[60] to treat the reaction of CH_3I with CH_3Na as a radical process; however, the polarisation of cyclobutane in the analogous reaction of 1,4-diiodobutane with sodium could not be observed.

The CIDNP of ^{19}F has been observed in the products of the reaction of n-butyl-lithium with p-fluorobenzyl chloride[56,57] and pentafluorobenzyl chloride[57]; in both cases, the reaction products are the corresponding symmetrical diphenylethanes and phenylpentanes (the product ratio $R_2' : RR' = 1 : 5$ for the former reaction and 1 : 6 for the latter, as shown by the NMR spectra); intense polarisation was observed for both products[56]. The p-nitrobenzyl radical has been detected in the reaction of BuLi with p-$NO_2C_6H_4CH_2Cl$.[57]

A not altogether comprehensible result was obtained in a study by Ward[46], who showed that there is no polarisation in the exchange reaction in the t-BuLi–n-BuLi system at −70°C, but on raising the temperature CIDNP is observed in the recombination and disproportionation products. However, in the EtLi–iso-PrI system at 40°C both iodides (EtI and iso-PrI) are polarised, undoubtedly due to the exchange process, which Ward treats as the interaction of R· and R′I, in conformity with Russell's mechanism (see below).

The observation of the polarisation of all the products formed in the reaction of RLi with R′X (the metal–halogen exchange, the "normal" Wurtz reaction, and the formation of radical disproportionation products) makes it possible to describe all these processes in terms of the SET mechanism.

Russell[61], who succeeded in showing that one electron transfer may occur in the Wurtz and exchange reactions even when the yield of RR′ is fairly high, attributes a general significance to this mechanism. In a study of the reaction of RLi with R′X by ESR using a flow system, whereby detection approximately 0.03 s after mixing the reactants is possible, Russell obtained direct proof of the primary formation of radicals. In the reactions of n-butyl-lithium with R′I (R′ = Et, n-Pr, n-Bu, n-Oct, or t-Bu), only the R′· radicals, which arise before the metal–halogen exchange takes place, i.e. from the iodide molecule, were observed. However, the spectra of certain bromides and $PhCH_2Cl$ revealed only the signal of the n-butyl radical, while both possible radicals were found in the reaction of s-BuLi with EtBr and of n-BuLi with CH_3I.

According to Russell, the results agree best with the following mechanism

$$RM + R'X \xrightarrow{k_1} R^{\cdot} + R''^{\cdot} + MX; \quad (1)$$

$$R^{\cdot} + R'X \xrightarrow{k_2} RX + R''^{\cdot}; \quad (2)$$

$$R''^{\cdot} + RLi \xrightarrow{k_3} R'Li + R^{\cdot}; \quad (3)$$

$$R''^{\cdot} + R^{\cdot} \xrightarrow{k_4} \text{alkanes and alkenes}. \quad (4)$$

The particular radical detected in the spectrum depends on the rates of stages (2) and (3). On the other hand, the rates are naturally determined by the nature of the radicals R· and R′· and the anion X^-. For iodides (R = Bu and R′ = Et or Pr), the rate of stage (2) exceeds that of stage (3) and the radicals R′· have been observed. When $X^- = Br^-$ or Cl^-, the rate of this stage diminishes and only R· or a mixture of R· and R′·¶ ($k_2 \simeq k_3$) is observed. For allyl bromide, the spectrum reveals the presence of allyl radicals only. Russell states that reactions (2) and (3) constitute the possible mechanism of the metal–halogen exchange. However, he does not rule out the possibility of some contribution by the heterolytic process in such reactions.

It is seen from the examples quoted that the composition of the products formed depends on the nature of R, R′, X, and M. The result is determined to a significant extent by the nature of the solvent. In the study of Eastham and Gibson[39] already mentioned, it was shown that in a non-polar medium (hexane) butyl-lithium reacts with R′X via a hydride reduction mechanism, while in ether the usual Wurtz reaction takes place. The change in the mode of reaction as a function of the nature of the solvent has been illustrated[63] by a study of the reaction of butyl-lithium with benzyl chloride. In hexane and ether, the authors observed the formation of n-alkylbenzene and bibenzyl, while in THF *trans*-stilbene was found (20%). A significantly higher yield of the dimerisation products RR′ in the Wurtz reaction has been observed in benzene in relation to ether[64]. However, an increase in solvent polarity usually leads to an increase of the yield of the Wurtz reaction product. Thus it has been shown in a recently published study[65] that in the hexane : THF = 1 : 5 mixture the reaction of n-butyl-lithium and n-octyl-lithium gives satisfactory yields of the hydrocarbons RR′ even with aryl halides.

¶ The problem of the mechanism of the reaction between R and R′X can also be treated from different standpoints: as an S_N2 reaction involving the halogen atom or as the reduction reaction

$$R^{\cdot} + R'X \longrightarrow R^+ + (R'X)^{\cdot -} \longrightarrow RX + R''^{\cdot},$$

which naturally proceeds more readily with iodides. The results agree with those of Evans and Szwarz[62], who showed that the methyl radical abstracts the halogen from MeI 7×10^3 faster than from MeBr. This also applies to the reaction of R′· with RLi.

By tradition it has come to be accepted that an increase in the polarity of the C–M bond under the influence of the solvent facilitates the heterolytic process, which is indicated by the increase of the yield of RR', and that the radical mechanism can be replaced by a heterolytic mechanism under the influence of the solvent[45,66-68]. Thus a detailed study has been made[66] of the reaction of butylmagnesium iodide with R'X in cumene or in higher alkanes and it has been shown that the hydrocarbons RH, R'H, R(–H), and R'(–H) are formed in all cases, while in cumene the formation of appreciable amounts of bicumenyl is observed in addition. On passing to DME, the situation changes sharply. The simplest RMgX and R'X readily enter into the "normal" Wurtz reaction in DME, although even in ether this reaction is not at all characteristic of these substances. The authors believe that, on passing from hydrocarbon solvents to DME, the mechanism of the reactions of organomagnesium compounds with R'X changes from radical to heterolytic.

Here one should note that the exchange reaction R'X + RM → R'M + RX, which is well known for the more reactive organolithium compounds, is believed to be generally atypical in the series of organomagnesium compounds and takes place only when the difference between the electronegativities of the groups R and R' is large[21]. However, in strongly solvating solvents such radical exchange does occur also for the simplest alkyl or aryl-magnesium halides and alkyl halides[67]. For example, the degree of exchange in the reaction of n-$C_5H_{11}MgBr$ with CH_3I varies from 5.7% (1 h, 0°C, in ether) to 38% in DME. Since the ease of exchange increases with increase of the solvating capacity of the solvent, the authors treat this reaction as heterolytic. However, one cannot rule out the possibility that not only the amount of ionic character of the C–M bond but also the ability of the organometallic compounds to behave as an electron donor is altered by the solvent. From the standpoint of the unified SET mechanism, the influence of the solvent on the composition of the products (but not on the rate of reaction) should be manifested as a result of a change in the nature of the "cage" enclosing the radical-ion pairs formed and not as a result of the change in the nature of the dissociation of the C–M bond. Unfortunately, nothing is as yet known about the nature of this cage and about its influence on the stability of the radical-ion pair.

Thus, in recent years, particularly after the publication of CIDNP data and Russell's study[61] concerning the detection of radicals in the reactions of simple alkyl halides with alkyl-lithium, there has been a tendency to treat the exchange and Wurtz reactions from the standpoint of the radical mechanism. However, we believe that the conclusion that there is a single mechanism for all the processes involving the SET stage may prove to be premature. We have been led to this conclusion mainly by analysis of stereochemical data.

IV. STEREOCHEMISTRY OF THE EXCHANGE AND WURTZ REACTIONS

In the first place we shall consider the results obtained in the study of the stereochemistry of the exchange reactions. Unfortunately the stereochemistry of such processes, occurring at a tetrahedral unstrained carbon atom, has been hardly investigated. The only available stereochemical result for reactions of this kind is apparently the partial retention of configuration found by Letsinger in the s-butyl-lithium–optically active 2-iodo-octane system[69]. Only when the reaction was carried out at –70°C (in a petroleum ether–ethyl ether mixture) was the author[69] able to obtain the optically active 2-lithio-octane, but its activity was lost on raising the temperature to 0°C (after carboxylation, the acid proved to be fully racemic).

One cannot rule out the possibility that the racemisation of the organometallic compounds formed in the metal–halogen exchange in fact accounts for the formation of the racemic products RR' in the reactions of R'Hal with simple alkyl derivatives of metals (see below), particularly if one bears in mind that the reactions are frequently carried out at fairly high temperatures (0°C and above). For example, Wittig[70] obtained virtually inactive 2,3-diphenylbutane in the reaction of the optically active α-bromoethylbenzene with phenyl-lithium in ether and explained its formation by the exchange reaction of the bromide with PhLi and the subsequent Wurtz reaction between $Ph-\underset{\displaystyle Li}{\underset{|}{C}}HCH_3$ and $PhCH(Br)CH_3$. Thus, in principle, the reaction can take place with retention of configuration. The possibility of the retention of configuration in the metal–halogen exchange reaction has been confirmed also by the finding that the exchange takes place readily between 1-bromotriptycene and butyl-lithium (with formation of 1-lithiotriptycene)[50], i.e. in the system where the retention of configuration is predetermined by the structure of R'X and where processes of the S_N2 type, occurring with retention of configuration, are impossible.

The organolithium derivatives of the vinyl and cyclopropyl series are more stable, so that the stereochemistry of the metal–halogen exchange in such cases has naturally been investigated in greater detail. The organolithium compounds were not isolated or a configuration assigned in any instant and the stereochemical course of the reaction was inferred from the configuration of their conversion products, for example after carboxylation, Li–H exchange, the cleavage of $HgCl_2$, I_2, or Br_2, etc. (it is assumed that all these reactions are of the S_N2 type and take place with retention of configuration). Thus investigations have shown that all the reactions investigated take place with retention of configuration (Table 1), which is evidence against the involvement of free radicals in the exchange reactions. The retention of configuration in the exchange reactions of the *cis*- and *trans*-isomers of the cyclohexyl derivatives of lithium with methyl iodide and bromobenzene[71] also supports these conclusions.

We shall now consider the stereochemical data available for the Wurtz reactions involving organosodium, organolithium, and organomagnesium compounds. The results are compiled in Tables 2–4. The principal stereochemical results in Tables 2–4 may be summarised as follows. The reactions of organosodium and organolithium derivatives of the benzyl and allyl type with R'X proceed with preferential and sometimes complete inversion of configuration. However, in the reactions of the corresponding organomagnesium compounds, the percentage racemisation increases appreciably. On the other hand, the interaction of simple alkyl derivatives of sodium and lithium with RX' results in racemisation, the only exception apparently being the reaction of lithium diphenyl cuprate with s-butyl bromide, which takes place with inversion of configuration to the extent of 84–92%†.[81]

† Naturally the mechanisms of the reactions of Ph_2CuLi and simple RLi and RNa with R'X are the same.

From general considerations, the stereochemical results of radical reactions presumably involve racemisation, possibly with partial retention of configuration. The retention of configuration under these conditions may be due to the recombination of radicals in the cage or the presence of a barrier to inversion. Only in the case of a stable radical, with a fairly high inversion barrier, can one expect the preferential retention of configuration. This probably actually accounts for the observed retention of configuration in the reaction of bromo-derivatives of the vinyl series with lithium dimethyl- or diphenyl-cuprates [81,82].

Table 1. Stereochemical results of the reactions of RLi with R′X.

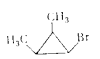
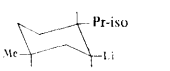
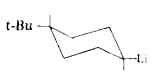
RLi	R′X	Stereochemical result	References
s-BuLi	2-IC_8H_{17}	20% retention, 80% racemisation	69
n-BuLi	*cis*- and *trans*- p-ClC_6H_4(Ph)C=C(Br)Ph	retention	72
»	*cis*- and *trans*- PhCH=C(Br)Ph	retention	73, 74
»	*cis*- and *trans*- 	retention	75
		retention	75
	cis- and *trans* 	retention	76
»			
»			
	CH_3I	90% retention	71
	PhBr	85% retention	71
			

Table 2. Stereochemical results of the reactions of RNa with R′X.

RNa	R′X	Yield of RR′, %	Stereochemical result	References
C_2H_5Na	2-BrC_8H_{17}	25	90% racemisation	35
n-C_4H_9Na		35	total racemisation	36
2-NaC_8H_{17}		—	ditto	37
s-C_4H_9Na	s-C_4H_9Br	—	"	37
C_2H_5Na	2-ClC_8H_{17}	—	inversion, 20% racemisation	77
2-NaC_8H_{17}	»	—	partial inversion, exact assignment of configuration unavailable	37
Ph_2CHNa	PhCH(Cl)CH_3	—	exact assignment unavailable, but only slight racemisation observed	78
$PhCH_2Na$	s-C_4H_9Br	65—69	74% inversion, 26% racemisation	5
»	2-BrC_8H_{17}	80	70% inversion, 30% racemisation	5
CH_2=$CHCH_2Na$	»	83	79-81% inversion, 13-21% racemisation	6
»	PhCH(Cl)CH_3	—	inversion (exact assignment unavailable)	79
$NaCH(COOEt)_2$	2-BrC_8H_{17}	—	inversion	34

Naturally the inversion of configuration cannot be interpreted from the standpoint of the radical mechanism. For this purpose, one would have to postulate the occurrence of S_N2 reactions which would result in inversion of configuration and which would include attack by R· on the carbon atom:

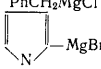
$$R^{\cdot} + R'X \rightarrow RR' + X^{\cdot}.$$

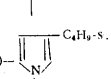
Table 3. Stereochemical results of the reactions of RLi with R′X and of R_2CuLi with R′X.

RLi or R_2CuLi	R′X	Yield of RR′, %	Stereochemical result	References
n-C_4H_9Li	s-C_4H_9Br	37	98% racemisation	80
PhLi	2-BrC_8H_{17}	30	racemisation	9
n-C_3H_7Li	»	30	racemisation	9
$PhCH_2Li$	s-C_4H_9Br	58	100% inversion	7
»	2-BrC_8H_{17}	85	ditto	7
CH_2=$CHCH_2Li$	»	68	108% inversion	
»	»	87—95	inversion	9
»	2-ClC_8H_{17}	59	92% inversion	7
»	PhCH(Cl)CH_3	34—39	29-38%* inversion	7
Ph_2CHLi	2-ClC_8H_{17}	48	100% inversion	7
CH_2=$CHCH_2Li$	2-$C_8H_{17}SO_3C_6H_4CH_3$	60	93% inversion	8
»	2-IC_8H_{17}		90% inversion	
$PhCH_2Li$	»		90—93% inversion	8
»	2-$C_8H_{17}SO_3C_6H_4CH_3$		90-93% inversion	
Ph_2CuLi	s-C_4H_9Br		84-92% inversion	81
»	*cis*- and *trans*-bromostyrenes	98	retention	81
$(CH_3)_2CuLi$	*trans*-bromostyrene	81	retention	82
»	*cis*-bromostyrene	»	retention	
»	*cis*-1-bromo-4-t-butylcyclohexane	45% *trans*-, 41% *cis*-	non-stereospecific	82

* The authors believe that the low percentage inversion may be due to the metallation of the hydrocarbon RR′ and the racemisation of the carbanion.

Table 4. Stereochemical results of the reactions of RMgX with R′X.

RMgX	R′X	Yield	Stereochemical result	References
CH_3MgI	PhCH(Cl)C_2H_5	—	racemisation	83
CH_2=$CHCH_2MgBr$	2-BrC_8H_{17}	78	79-87% inversion, 13-21% racemisation	6
»	PhCH(Cl)CH_3	—	low percentage inversion, exact assignment unavailable	79
PhCH(MgCl)CH_3	PhCH(Cl)CH_3	—	racemisation	84
$PhCH_2MgCl$	2-BrC_8H_{17}	17	91% racemisation	6
	s-C_4H_9Br	30% (I)* 12% (II)	100% inversion	85

* (I)  (II) 

Furthermore, it is known [79] that such processes involve as a rule terminal atoms [Hal, M(I)]:

$$R^{\cdot} + R'X \rightarrow RX + R'^{\cdot}.$$

This stereochemical result of the reactions of RNa with R′X in fact forced Le Goff et al. [34] to conclude as early as

1958 that "there is almost no doubt about the ionic mechanism of the reaction".

Another stereochemical result, namely racemisation, which has been observed for many reactions of RLi and RNa with R'X, can be interpreted fairly simply by the radical mechanism. However, in this case there is a possibility also of an alternative explanation associated with the occurrence of metal–halogen exchange processes. One may suppose that the exchange processes involving simple alkyl derivatives of lithium and sodium proceed more readily than for the benzyl or allyl derivatives and this is the reason for the formation of the racemic products RR' (RLi or RNa, formed as a result of the exchange reaction, racemise; see above). On the other hand, if it is assumed that the exchange processes proceed via a radical mechanism, then evidently they must be accompanied by "losses" associated with the reactions of the radicals liberated from the cage. Indeed the yields of RR' are extremely low in the reactions of R'X with simple alkyl derivatives of lithium and sodium, while in the case of the allyl and benzyl derivatives they are nearly quantitative. However, it is at present extremely difficult to reach any conclusions, since an increase in the reactivity of RM, like that of R'X (for example on passing from chlorides to iodides), should increase the rates of both processes (although possibly to different extents).

On the other hand, it is difficult to account for data obtained for the Wurtz reactions involving RMgX from the standpoint of an ionic S_N2 mechanism. Exchange processes are known to be less typical for organomagnesium compounds than for organolithium or organosodium compounds[21,67]. Nevertheless, preferential racemisation, even in reactions with R'X incapable of reacting via the S_N1 mechanism although the yield of RR' are in fact highest in processes of this type, is often the stereochemical result of reactions involving allyl- or benzyl-magnesium halides. It is noteworthy that the available data for the stereochemistry of the Wurtz reaction with participation of RMgX are limited to only a few examples (Table 4).

It is evident from the data described that the Wurtz reaction and the metal–halogen exchange reaction cannot be described within the framework of a single mechanism, particularly since a change in the nature of M, R, R', and the halogen may alter the process mechanism. We shall now consider the possible mechanisms of the exchange and Wurtz reactions in the light of the available data (particularly stereochemical data) for these processes.

V. POSSIBLE MECHANISMS OF THE EXCHANGE REACTIONS

1. The mechanism proposed by Wittig to explain the ease of the exchange of the bridgehead halogen[50], which involves nucleophilic attack on the halogen (cationoid abstraction of the halogen) and which may be regarded as a mechanism involving electrophilic substitution at the carbon atom in R'X:

$$R'X + RM \rightarrow [R' : \ddot{X} : \; : R]^- M^+ \rightarrow RX + R'M.$$

The stereochemical result of such a process should be retention of configuration. This mechanism is frequently invoked, particularly for reactions of organobimetallic compounds with R'X, to explain the retention of configuration in exchange reactions. However, exchange processes are as a rule accompanied by the formation of alkanes and alkenes, which cannot be explained within the framework of this mechanism (provided, of course, that the exchange reactions and the reactions involving the formation of these hydrocarbons have a common rate-limiting stage).

2. Electron transfer with formation of a radical-ion pair in which a redistribution of radicals may occur:

$$RM + R'X \rightarrow \begin{bmatrix} R^{\cdot} & M^+ \\ R'^{\cdot} & X^- \end{bmatrix} \rightarrow RX + R'M.$$

The formation of alkanes (RH, and R_2 or R'_2) and alkenes can be explained from the standpoint of this mechanism by the liberation of R' and R'' radicals from the cage. If it is postulated that the radical distribution process takes place in the cage, one can thus account for the observed retention of configuration. However, in consequence of the inversion of the radicals in the cage, even in this case the process can occur with partial or even preferential racemisation.

3. The radical chain mechanism proposed by Russell[61]:

$$R^-M^+ + R'X \rightarrow R^{\cdot} + R'^{\cdot} + MX; \quad (1)$$

$$R^{\cdot} + R'X \rightarrow RX + R'^{\cdot}; \quad (2)$$

$$R'^{\cdot} + RM \rightarrow R'M + R^{\cdot}; \quad (3)$$

$$R^{\cdot} + R'^{\cdot} \rightarrow RR' + \text{alkanes and alkenes.} \quad (4)$$

This mechanism probably gives at the present time the best explanation of the exchange process [stages (2) and (3)]. The formation of different hydrocarbons can be understood within the framework of this mechanism, although the stereochemical result of reactions (2) and (3) should be racemisation. In a few instances one can probably expect also the retention of configuration, for example for radicals of the vinyl and cyclopropyl series which have high inversion barriers. There is no doubt that the free-radical mechanism appears particularly attractive for the exchange reaction, which is in essence an oxidation-reduction process. However, one cannot explain within the framework of this mechanism the results of Mechinger's study, which has become a classical (and so far unique) example of this kind, showing the possibility, in principle, of the retention of the stereochemical configuration in exchange reactions involving an sp^3-hybridised uncharged carbon atom[69]. On the other hand, the observation of CIDNP in alkyl halides together with the observation of the polarisation of alkanes and alkenes shows that these products are formed via a mechanism involving an SET stage or a chain radical process. There remains only one possibility—to assume that in reality a combination of mechanisms [(1) and (2) or (2) and (3)] obtains. There has been only one investigation which throws doubt on the SET mechanism of radical exchange reactions (in halogen–metal systems). This is the study of Ward and coworkers[46] (whose results have been published in the abstracts of reports at the conference in Belgium in 1971), where the authors failed to observe CIDNP in the reaction of t-BuLi and n-BuI at −70°C involving exchange, but did observe CIDNP in the disproportionation products formed on raising the temperature, i.e. in the products arising under the conditions of the Wurtz reaction.

VI. POSSIBLE MECHANISMS OF THE WURTZ REACTION

1. The heterolytic mechanism of the S_N2 type‡

$$RM + R'X \rightarrow [M^{\delta+}R^{\delta-} \ldots R'^{\delta+}X^{\delta-}] \rightarrow MX + RR'.$$

The stereochemical result of this process is inversion of configuration. This mechanism has been frequently invoked in studies on the reactions of benzyl and allyl derivatives of lithium and sodium, since preferential inversion of configuration has in fact been observed in such cases. The reactions of lithium dimethyl- and diphenyl-cuprates with R'X also take place with inversion of configuration [81,82], probably owing to their pronounced nucleophilic properties in relation to the carbon atom.

This mechanism is probably also valid for the reactions of simple alkyl derivatives of sodium and lithium with R'X, which take place with racemisation, if it is assumed that the racemisation is a result of the loss of configuration by the organometallic compound RM during the exchange process and is not a consequence of the Wurtz reaction. This hypothesis is particularly likely, because simple alkyl derivatives of lithium and sodium should show the greatest tendency towards exchange reactions by virtue of their basicity, which is confirmed by the formation of R_2 and R'_2 together with RR' in these reactions, in contrast to the reactions of benzyl and allyl derivatives of sodium and lithium, where compounds RR' are sometimes formed in nearly quantitative yields. However, the stereochemical result (racemisation) in the reaction of optically active R'X with RMgX (even of the allyl and benzyl types) remains inexplicable within the framework of this mechanism. Exchange processes are not characteristic of these reactions, because the latter have been carried out in hydrocarbon media or in hydrocarbon–ether mixtures, where hardly any exchange processes occur. Unfortunately the stereochemical data obtained for Wurtz reactions involving RMgX are extremely limited.

A change in the nature of R'X can lead to a change from an S_N2 to an S_N1 mechanism, which involves attack by RM on the carbonium centre of the carbonium ion R'^+ of the corresponding ion pair R'^+X^-. Racemisation accompanied by inversion of configuration when the ion pair is involved should be the stereochemical result of this reaction. However, one should recall that such reactions are usually carried out in ethereal solvents or in ether–hydrocarbon mixtures, which hardly promotes the ionisation of the R'X molecule and the operation of an S_N1 mechanism. On the contrary, an increase of the electron-donating capacity of the solvent (for example on passing from ether to DME of the glymes) promotes the ionisation of the organometallic compound molecule.

2. The mechanism of the S_Ni type:

$$RM + R'X \rightarrow \left[\begin{matrix} R\text{—}M \\ \vdots \\ R'\text{—}X \end{matrix}\right] \rightarrow \left[\begin{matrix} R\cdots M \\ \vdots \\ R'\cdots X \end{matrix}\right] \rightarrow RR' + MX.$$

An attempt has been made to consider this mechanism for the Wurtz reaction of RNa with R'X; it is readily seen that it does not explain the formation of the observed products and stereochemistry, but it can obtain in reactions of covalent organometallic compounds, for example organomercury compounds (the reaction of RHgX or R_2Hg with R'X is discussed below). The stereochemical result of this reaction involves retention of configuration. However, when a fairly stable carbanion corresponds to the organic group R in the RM molecule, the rate-limiting stage of this process may become the ionisation of the RM linkage under the influence of nucleophilic coordination, i.e. the true mechanism is of the S_E1 type. The stereochemical result in this case may be racemisation, although one cannot rule out partial retention of configuration.

Finally one cannot rule out the possibility that both processes can involve electron transfer as a separate stage, which is rate-determining in an ionisation mechanism. The occurrence of SET in this instance would explain the formation of radicals in the reaction of Ar_2Hg with Ph_3CX (Beletskaya et al. [87]) and the CIDNP in the product Ph_3CCH_2Ar of the reaction of $(ArCH_2)_2Hg$ with Ph_3CX. [88] The stereochemical results of these reactions should involve retention of configuration or racemisation, but such data are so far unavailable in the literature.

3. Electron transfer as in the exchange reaction. When radicals recombine in the cage, one may expect the retention of configuration, but it is difficult to suppose that such recombination takes place only in the cage, particularly if one is dealing with fairly stable radicals of the allyl or benzyl type. On the other hand, one cannot explain within the framework of this mechanism the observed inversion of configuration which actually occurs in reactions involving RM of the benzyl or allyl type. The possible alternative explanation involving electron transfer in the oriented attack in the complex $[MR^{\delta-}\ldots R^{\delta+}'X]$§ lacks any supporting evidence at the present time.

4. The radical chain mechanism in which the Wurtz reaction product is formed on recombination of the radicals R· and R'·. For the usual radicals, the natural stereochemical result should be racemisation. Analysis of the possible reaction pathways showed that, in order to account for the inversion of configuration in the Wurtz reaction, the absence of radical stages must be postulated.

At first sight the heterolytic mechanism in both the Wurtz and the exchange reactions is supported also by the finding that both reactions are appreciably accelerated in highly solvating media and that under such conditions the yield of hydrocarbons RH, R(–H), etc. is in fact reduced, while their amount increases sharply in hydrocarbon media, where there are virtually no products of the Wurtz reaction proper. These results can also be interpreted in a different way. An increase in the electron-donating capacity of the solvent leads to an increase of the basicity (and nucleophilicity) of the RM molecule and probably to a

‡ The assignment of this reaction to processes of the S_N2 type is purely arbitrary. It could be just as successfully regarded as a reaction of the S_E2 type. In this case the assignment was made because the study of the stereochemistry of the reaction (on which attention has been mainly concentrated in this section) has been carried out on the optical or geometrical isomers of R'X. This applies also to mechanisms of the S_Ni and S_Ei types.

§ The formation of radicals has been recently demonstrated in a typical S_N2 reaction involving inversion of configuration. This enabled the authors to postulate that the transition state is a "hybrid" of the usual transition state of an S_N2 reaction and a radical pair [89]. On this hypothesis, it is indeed found that electron transfer should take place from "the rear". However, the authors failed to take into account the fact that a synchronous S_N2 mechanism cannot lead to the formation of different products (radicals and nucleophilic substitution products) from the same transition stage.

facilitation of the electron transfer process. On the other hand, these solvents can increase the stability of the radical-ion pair by solvation, as a result of which the radicals are less able to emerge from the cage.

Thus the observed characteristics of the Wurtz reaction cannot be explained within the framework of a single mechanism either. In order to account for the inversion of configuration, it is necessary to invoke a heterolytic pathway, while the retention of radicals (Russell's data[61]) and CIDNP in the recombination products requires a radical pathway. On the other hand, the ratio of the contributions of these pathways in each specific case constitutes an independent problem.

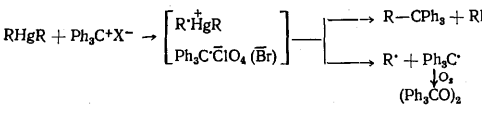
VII. REACTIONS OF OTHER ORGANOMETALLIC COMPOUNDS WITH ALKYL HALIDES

The formation of triphenylmethyl radicals has been demonstrated in a Wurtz-type reaction between organometallic compounds Ar_2Hg and triphenylmethyl bromide or perchlorate[87]. The ratio of the amounts of the Wurtz reaction products $ArCPh_3$ and triphenylmethyl peroxide depends strongly on the nature of the solvent and the substituent in the benzene ring of Ar_2Hg (Table 5).

Table 5. The yields of products in the reactions of Ar_2Hg with Ph_3CX.

p-X	Solvent	(Ph_3CO_2), %	*p*-$XC_6H_4CPh_3$, %	*p*-X	Solvent	$(Ph_3CO)_2$, %	*p*-$XC_6H_4CPh_3$, %
H	benzene	15	85	CH_3O	DCE	90	10
H	DCE	60	40	Cl	»	20	80

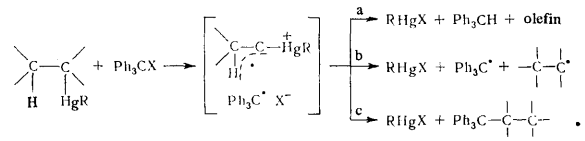
In this case one can also postulate the occurrence of two simultaneous processes (radical and heterolytic), one of which may predominate. However, bearing in mind that the change in the rate of reaction following the alteration of X is described by the Brown–Okamoto equation (σ^+), the hypothesis of a single mechanism in which the rate-determining stage is electron transfer appears to be more probable:



One can attempt to explain the observed behaviour by the properties of the radical-cation formed initially, the stability of which should decrease in the sequence $CH_3O > H > Cl$; the higher the stability of these species the greater the "freedom" and ability to emerge from the cage acquired by its partner in the radical-ion pair, i.e. triphenylmethyl. On the other hand, the rate of reaction increases in the sequence methylene chloride < CH_3CN < benzene; the yield of triphenylmethyl peroxide increases in the same sequence. It may be that the radical-ion pair in π-donor solvents is more stable and this is responsible for the higher degree of recombination of the radicals in the cage; in the case of DCE, the radicals are more capable of leaving the cage (in all the solvents the formation of $Ph_3C^\cdot$ has been detected by ESR in the absence of oxygen, but in benzene the yield of the radical is low).

The validity of the proposed mechanism is demonstrated directly by the observation of CIDNP in $RCPh_3$ in the reaction of triphenylmethyl bromide with benzylmercury bromides p-$XC_6H_4CH_2HgBr$ (X = H or CH_3) and dibenzylmercury in DCE and methylene chloride[88].

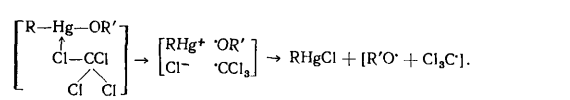
For alkyl derivatives of mercury containing a β-hydrogen atom capable of mobility as the hydride ion, the dominant mode of reaction with triphenyl methyl halides and perchlorates is known to be a hydride shift leading to triphenylmethane and not the formation of the Wurtz reaction products[90–92]. However, one may postulate that the elementary steps in the two outwardly different processes are of the same type. Indeed a considerable positive polarisation of the methine protons of triphenylmethane has been observed in the reactions of di-(n-butyl)- and di-(s-butyl)-mercury with Ph_3CX (X = Cl, Br, or ClO_4) in DCE.[93] On this basis, the following mechanism including the stage of one-electron transfer via the C–Hg bond to Ph_3CX has been postulated for the reactions under consideration:



In this mechanism triphenylmethane (pathway *a*) is a product of the abstraction of the β-hydrogen atom by the triphenylmethyl radical and not of the hydride shift as traditionally understood. The competing modes of reaction under these conditions are pathway *c* involving radical recombination in the cage and pathway *b* involving the liberation of the radicals from the cage, which becomes the main pathway when tri-(*p*-nitrophenyl)methyl bromide is used as the electrophilic agent (probably in consequence of the extremely high stability and low tendency towards recombination of the corresponding radical).

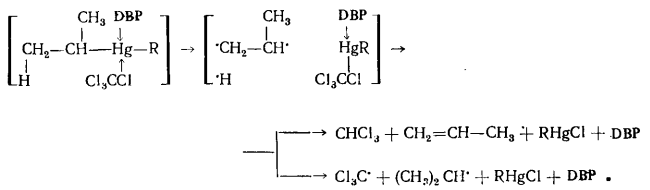
The SET mechanism in reactions of organomercury compounds with R'X may not be general and may obtain only in the specific case of the reaction with triphenylmethyl halides, owing to the ease of reduction of Ph_3CX and the formation of the stable triphenylmethyl radical. This hypothesis appears to be particularly valid, since in the general case the interaction of organomercury compounds with alkyl halides proceeds with extreme difficulty and a very low yield of RR'¶.

The mechanism including the SET stage has also been proposed for the reactions of mercury alkoxides RHgOR' with polyhalogenomethanes and the reactions of dialkyl- and diaryl-mercury compounds with CCl_4 in the presence of di-t-butyl peroxide (DBP).[94] The organomercury compounds R_2Hg as a rule react with CCl_4 or $CHCl_3$ under severe conditions (heating to the decomposition temperature of R_2Hg) and the process has a free-radical mechanism. Following the replacement of R by an alkoxy-group, the reaction proceeds under milder conditions:



¶ This situation is analogous to that occurring in S_N processes, where the usual S_N2 reactions take place with inversion of configuration and cannot be simulated by the reaction of Ph_3CBr with t-BuO-(or PhO^-), which leads to radicals only[95].

DBP acts in the same way; its introduction into the reaction of alkyl or phenyl derivatives of mercury greatly accelerates the latter (the optimal conditions obtain when $R_2Hg:DBP = 1:1$). On the other hand, DBP itself is consumed in the reaction to an extent not greater than 5%. According to the authors [94], the catalytic role of DBP reduces to the formation of a complex with R_2Hg, as a result of which the Hg–C bond is polarised to such an extent that R_2Hg becomes reactive in relation to CCl_4. When CCl_4 reacted with Alk_2Hg in the presence of equimolar amounts of DBP, considerable amounts of chloroform and propene (more correctly, 1,1,1,3-tetrachlorobutane formed from propene after the addition of CCl_4) were found in the reaction mixture. The authors explain the formation of these products by an intermolecular hydride shift, which they believe also proceeds via an electron transfer stage:



However, the data quoted by the authors [94] do not show that this is the only reaction pathway.

The formation of racemic products in the reactions of phenyl- or α-naphthyl-cadmium chloride with α-bromopropionate esters and the observation of an intense signal in the ESR spectrum when the reactants are mixed, suggests that these reactions have radical mechanisms [96].

CIDNP (both emission and positive polarisation) has been recently observed in the reaction of ethyl-lead with hexachlorocyclopentadiene and hexachloroacetone (the solvents) at 140°C: [97]

$$Et_4Pb + C_5Cl_6 \rightarrow Et_3PbCl,\ EtCl,\ EtC_5Cl_5,\ C_5Cl_5H,\ C_2H_4,\ (C_5Cl_5)_2.$$

Analysis of the polarisation signs indicates the occurrence of CIDNP in the singlet radical pair ($R^{\cdot}\ {}^{\cdot}Et$), but the authors do not regard electron transfer as the only possible reaction mechanism. Similar spectra have been observed in both solvents also for the reactions with $Et_2Pb(OAc)_2$ and Et_3PbOAc.

A wide variety of reactions involving organocopper compounds, including the reactions of RCu with organic halogeno-derivatives [98], have been investigated fairly vigorously in recent years. Some of these reactions have proved useful as regards syntheses; for example, the reactions of copper acetylides with a wide variety of halogeno-derivatives (acetylenic, vinyl, aromatic, etc.) are widely used for the synthesis of the corresponding hydrocarbons. In many instances thermally stable arylcopper compounds were introduced into the reaction with R'X. It is quite likely that some of these reactions proceed via a radical mechanism, but this problem has not been discussed in the literature. Furthermore, in many reactions, for example the reactions of arylcopper compounds with aromatic halides [99], a mixture of hydrocarbons is obtained, the formation of which can be readily explained by a radical mechanism. However, it is impossible to reach an unambiguous conclusion, because one cannot rule out the possibility that the formation of this mixture is associated with the occurrence of halogen–copper exchange processes, which has been demonstrated in many cases.

Somewhat more attention has been devoted (from the standpoint of the study of the mechanism) to the reactions of lithium (or magnesium) dialkyl- or diaryl-cuprates, which have higher thermal stabilities, with halogeno-derivatives [81,82]. The use of cuprates makes it possible to obtain high yields of the hydrocarbons RR' in reactions with primary and even secondary RHal or ROTos (70–100%).

As already mentioned above, the reaction of lithium diphenyl- and dimethyl-cuprates with s-butyl bromide takes place preferentially (to the extent of 84–92%) with inversion of configuration, which shows that it proceeds via an S_N2 mechanism [81]. Similarly a 100% inversion of configuration is observed in the reaction of lithium diphenylcuprate with (+)-2-(s-butyl)toluene-p-sulphonate or ethanesulphonate in ether [100]. However, the reactions of cuprates with halogeno-derivatives of the vinyl series to form RR' proceed with retention of geometrical configuration, which is clear evidence against an S_N2 mechanism. According to Whitesides et al., [81] this mechanism is also relatively unsuitable for the explanation of the ease of reaction of lithium diphenylcuprate with aromatic halides (it is striking that the reaction may be regarded as a variant of the Ullmann reaction, for which both oxidation-reduction and heterolytic [101] mechanisms have been proposed). There is no doubt that, as in the reactions of organomagnesium and organolithium compounds, there may be a change of mechanism or a change in the contribution of the radical or heterolytic reaction pathway in the series of different cuprates, depending on their nature and that of R'X.

VIII. REACTIONS OF ORGANIC DERIVATIVES OF TRANSITION METALS WITH ALKYL HALIDES

The ability of certain transition metal complexes to undergo oxidative addition reactions (which includes the reactions with R'X) constitutes the basis of their catalytic activity in many processes, such as the homogeneous hydrogenation of unsaturated compounds, the oxidation of alkanes, etc., and also reactions involving the dissociation and reformation of carbon–carbon bonds.

The interaction of transition metal complexes with alkyl halides constitutes one of the most interesting methods for the formation of a carbon–metal σ-bond [102,103]. The reaction can proceed as oxidative addition, in which the state of oxidation of the metal and its coordination number change by two units (two-electron oxidation):

$$L_nM + R'X \rightarrow L_nM\begin{matrix}R'\\X\end{matrix},$$

where L is the ligand. In the presence of a fairly stable group to be eliminated from the alkylating agent (CH_3SbF_6, CH_3SO_3F), only one fragment R' of the R'X molecule may add on [104,105] with formation of an alkylmetal cation, for example $[Pt(PPh_3)Me]^+$.

We shall naturally consider only reactions in which complexes of organic derivatives of metals are involved. The number of such reactions is small. The products of the addition of alkyl halides have been isolated for platinum(II) derivatives [106]; on heating, the complex decomposes with elimination of ethane:

$$[MePt(PEt_3)_2]I \overset{MeI}{\rightleftarrows} [Me_2PtI_2(PEt_3)_2] \xrightarrow{100^\circ} Me{-}Me + I_2Pt(PEt_3)_2.$$

It is postulated that the exchange of the *o*-tolyl group for methyl in the reaction[107]

$$(o\text{-MeC}_6\text{H}_4)_2\,\text{Pt}\,(\text{Py})_2 \xrightarrow{\text{MeI}} (o\text{-MeC}_6\text{H}_4)_2\,\overset{\text{Me}}{\underset{\text{I}}{\text{Pt}}}\,(\text{Py})_2 \rightarrow$$

$$\xrightarrow{115^\circ} o\text{-MeC}_6\text{H}_4\text{I} + (o\text{-MeC}_6\text{H}_4)\,(\text{Me})\,\text{PtI}_2\,(\text{Py})_2$$

proceeds via an intermediate of this kind.

The stereochemistry of the addition of MeI and CF_3I to platinum complexes, for example to *cis*-$Pt(Me_2)L_2$, has been studied[108]. The oxidative addition of methyl iodide to the triphenylphosphine complex of methylgold(I) proceeds via Me_2AuIL and the subsequent exchange of the alkyl halide with MeAuL gives a trimethylgold complex[109,110], which undergoes reductive elimination with formation of ethane:

$$\text{MeAuL} + \text{MeI} \underset{a}{\rightarrow} \text{Me}_2\text{AuIL} \xrightarrow[b]{\text{MeAuL}} \text{Me}_3\text{Au}^{\text{III}}\text{L};$$

$$\text{Me}_3\text{Au}^{\text{III}}\text{L} \underset{c}{\rightarrow} \text{Me—Me} + \text{MeAu}^{\text{I}}\text{L}.$$

Thus the complex MeAuL behaves as the catalyst in the dimerisation of alkyl groups[111]. A significant difference has been observed between the reactivities of the complexes in relation to oxidative addition (*a*) and alkyl exchange (*b*) processes as a function of the nature of the ligand. The complex Me_3AuPMe_3 is much more stable than Me_3AuPPh_3, so that it enters into a slow methyl–iodine exchange reaction with $IAu(PMe_3)$ or CH_3I without undergoing elimination.

It follows from the above mechanism that the oxidative addition reactions are assumed to have a polar mechanism. However, the possibility of a radical reaction pathway has been recently discussed in relation to an inorganic iridium(I) complex[112–114]. A free-radical chain mechanism is proposed for the process on the basis of the inhibiting effect of radical "traps" and the loss of configuration of the α-carbon centre in the reaction of $IrCl(CO)L_2$ with optically active ethyl α-bromopropionate[114].

There is another one-electron mechanism of the oxidation of transition metal complexes by alkyl halides:

$$2\text{L}_n\text{M} + \text{R'X} \rightarrow \text{L}_n\text{MR'} + \text{L}_n\text{MX}.$$

In this case the reaction undoubtedly proceeds via a free-radical mechanism:

$$\text{L}_n\text{M}^{\text{II}} + \text{R'X} \xrightarrow{\text{slow}} \text{L}_n\text{M}^{\text{III}}\text{X} + \text{R}^{\cdot};$$

$$\text{R}^{\cdot} + \text{L}_n\text{M}^{\text{II}} \xrightarrow{\text{fast}} \text{L}_n\text{M}^{\text{III}}\text{R'}.$$

The reactions involving the oxidation of iron(II) to iron(III) in porphyrins[115] and haemoglobin[116] by alkyl halides may serve as an example:

$$\rangle\text{Fe}^{\text{II}} + \text{R'X} \rightleftarrows \rangle\text{Fe}^{\text{II}}\,(\text{XR'}) \rightarrow \rangle\text{Fe}^{\text{III}}\text{X} + \text{R}^{\cdot}.$$

The fate of the radical depends on its nature; alkyl, benzyl, and propargyl radicals recombine to form R'_2. A further reduction of the radical with formation of alkanes is possible:

$$\text{R}^{\cdot} + \rangle\text{Fe}^{\text{II}} + \text{H}^{+} \rightarrow \rangle\text{Fe}^{\text{III}} + \text{R'H},$$

The alkanes are formed almost quantitatively when bromomalononitrile and diethyl bromomalonate are used as the alkyl halides[116].

The reactions of alkyl halides with cobalt[117,118] and chromium[119] complexes, leading to the formation of organic derivatives of these metals, have similar mechanisms. Generally speaking, these reactions involve the reduction of alkyl halides by metal salts (and not by organometallic compounds) and for this reason they are outside the scope of the review. We shall only mention that reactions of this kind include the alkylation of cobaloximes[120–122]:

$$2\text{Co}^{\text{II}}\,(\text{dmg})_2\,\text{L} + \text{R'X} \rightarrow \text{XCo}^{\text{III}}\,(\text{dmg})_2\text{L} + \text{R'Co}^{\text{III}}\,(\text{dmg})_2\,\text{L},$$

where dmg is dimethylglyoximate and L = Py, PPh_3, etc., and the reactions of R'X with vitamin B_{12S} [a cobalt(I) complex][123,124], which are biochemically important.

However, it is believed[122,123] that, in contrast to the reactions of $Co(CN)_5^{3-}$ (Halpern and Maher[117]) and cobaloximes[120], those of R'X with vitamin B_{12S} proceed as classical nucleophilic substitutions and do not involve electron transfer. This view is based on data for the influence of the nature of R' on the course of the reaction. It is interesting to note that, according to the results of these investigations, vitamin B_{12S} is the most powerful nucleophile known (a supernucleophile[123]).

The stereochemical result of the reaction obtained in the alkylation of cobalt(I) cobaloximes by *cis*- and *trans*-1,4-dibromocyclohexanes, namely complete inversion at the carbon centre, also suggests that this process involves bimolecular nucleophilic S_N2 substitution[125].

IX. REACTIONS OF ORGANOBIMETALLIC COMPOUNDS† WITH ALKYL HALIDES

It is useful to examine briefly also data obtained for reactions of organobimetallic derivatives with alkyl halides, since in this case it is possible to note the same trend in the development of ideas concerning the reaction mechanism and the same difficulties in the determination of the mechanism which arise in the analysis of the results of studies on the reactions of RM with R'X. It is noteworthy that the reactions of $(R_{n-1}E_m)M$ with halogeno-derivatives constitute one of the methods for the formation of a C–transition metal σ bond.

Dessy et al.[126] investigated the reactivities of a series of compounds of the type $R_{n-1}E^-Bu_4N^+$ (where E are various Group IV and V metals and non-metals as well as transition metals, for example Fe, Cr, W, Mn, etc.) in relation to alkyl halides (MeI, EtBr, and iso-PrBr) in DME. The anions $R_{n-1}E^-$ were obtained via the electrochemical reduction of the corresponding derivatives, usually compounds of the type $(R_{n-1}E)_2$. Since no hydrocarbons of the type RH and R(–H) [or compounds of the type $(R_{n-1}E)_2$], which might have indicated a radical reaction mechanism, were detected in the products, the authors regarded the reaction as an S_N2 type process and the values of k_2 as a measure of the nucleophilic properties of the corresponding anions $R_{n-1}E^-$. However, the yields of bibenzyl (a "side" product) reached 47% in the reaction of trimethylsilylsodium with benzyl chloride, while the reactions of Me_3SiNa with butyl halides produced fairly large amounts of butane, the yield of which increased sharply on passing from the chloride to the bromide and to the iodide[127]. According to the authors[128], these results suggest the possibility of electron transfer with formation of radicals.

When triethylgermyl-lithium was allowed to react with chlorotriphenylmethane in benzene, the formation of the

† Any compounds of the type $(R_{n-1}E^-)_mM^+$, where *n* is the valence of the element E, which may be both a metal or a non-metal, and *m* is the valence of the metal M, we have defined arbitrarily as organobimetallic derivatives.

triphenylmethyl radical was observed (13%), its yield reaching up to 33% after the addition of ether to the reaction mixture. Other reaction products were triethyl(triphenylmethyl)germane (63%) and hexaethyldigermane. The authors explained the results from the standpoint of the mechanism involving electron transfer from triethylgermyl-lithium to triphenylmethyl chloride[127,129]:

$$Et_3GeLi + Ph_3CCl \rightarrow \begin{bmatrix} Li^+ \cdot GeEt_3 \\ Cl^- \cdot CPh_3 \end{bmatrix} \rightarrow LiCl + Ph_3C^\cdot + Et_3Ge^\cdot.$$

The same mechanism apparently obtained also in the reaction of bis(triethylgermyl)cadmium with triphenylmethyl chloride in toluene[127,129]. In this case the reaction is a multistage process. The first, exothermic stage involves the formation of the triphenylmethyl radical (according to ESR data). In the second stage, which is completed in several days at 20°C, metallic cadmium is formed. According to the authors, the exothermic stage involves electron transfer from $(Et_3Ge)_2Cd$ to Ph_3CCl:

$$(Et_3Ge)_2Cd + Ph_3CCl \rightarrow \begin{bmatrix} Et_3GeCd^+ \cdot GeEt_3 \\ Cl^- \cdot CPh_3 \end{bmatrix} \rightarrow Ph_3C^\cdot + Et_3GeCdCl + Et_3Ge^\cdot,$$

$$2Et_3Ge^\cdot \rightarrow (Et_3Ge)_2 \quad (48\%);$$

$$Ph_3C^\cdot + Et_3Ge^\cdot \rightarrow Et_3GeCPh_3 \quad (28\%).$$

The fact that the organobimetallic derivatives enumerated readily reduce compounds such as naphthalene (Me_2SiNa), tetracyanoethylene, and *o*- and *p*-chloranils, i.e. typical electron acceptors, is regarded as evidence in support of the likelihood of the SET mechanism in these reactions[127-129]. Nor is a possibility of processes of the S_N2 type complicated by exchange processes ruled out. For example, the products found in the reaction of Et_3GeLi with triphenylmethyl chloride can be accounted for equally successfully by the following mechanism:

$$Et_3GeLi + Ph_3CCl \rightarrow Et_3GeCPh_3 + LiCl;$$

$$Et_3GeLi + Ph_3CCl \rightarrow Et_3GeCl + Ph_3CLi;$$

$$Et_3GeLi + Et_3GeCl \rightarrow (Et_3Ge)_2 + LiCl;$$

$$Ph_3CCl + Ph_3CLi \rightarrow 2Ph_3C^\cdot + LiCl.$$

However, for the analogous mercury derivative $(Et_3Ge)_2Hg$, the authors give preference to a heterolytic four-centre mechanism, assuming that unstable bis(triphenylmethyl)mercury is formed in the reaction as an intermediate:

$$(Et_3Ge)_2Hg + 2Ph_3CCl \rightarrow 2Et_3GeCl + (Ph_3C)_2Hg \downarrow 2Ph_3C^\cdot + Hg.$$

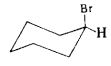
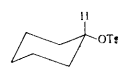
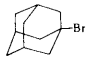
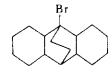
The reaction products are in fact mercury (93%), chlorotriethylgermane (68%), and hexaphenylethane‡ (91%). Hexaethyldigermane and triethyl(triphenylmethyl)germane could not be detected in the reaction mixture[129]. The same four-centre mechanism has been proposed also for the reaction of $(Et_3Ge)_2Hg$ with simple alkyl or aryl halides[127-131] and for the reaction of $(Me_3Si)_2Hg$ with aryl halides[133]. The authors of the last investigation believe that virtually all the products can be accounted by an S_Ni mechanism; if the radical reaction pathway does occur, its contribution is very small. The reaction of triphenylstannylsodium with 1-bromoadamantane in liquid ammonia probably proceeds via a radical mechanism[134].

A mechanism including the SET stage has been proposed for the reaction of sodio- and potassio-dibutylboron with alkyl halides (MeI, n-HepI, $PhCH_2Br$, and $PhCOCH_2Br$). The formation of a mixture of RH, R_2, and Bu_3B was observed in all cases; the yield of the product of the Wurtz reaction proper was vanishingly small under these conditions (< 1%).[135]

X. STEREOCHEMISTRY OF REACTIONS OF ORGANOBIMETALLIC COMPOUNDS WITH ALKYL HALIDES

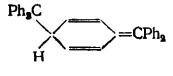
There have been several studies on the stereochemistry of reactions of organobimetallic derivatives of Group IV elements with alkyl halides (Table 6).

Table 6. Stereochemical data obtained for the reactions of organibimetallic compounds with various R'X.

$R_{n-1}E^-M^+$	R'X	Solvent	Stereochemical result	Refs.
Ph_3SiLi	s-C_4H_9Br	THF	51% inversion	136
Ph_3GeNa	»	NH_3(liq.)	67% inversion	»
Ph_3SnNa	s-C_4H_9Cl	DME	90% inversion	»
Ph_3SnNa	s-C_4H_9Br	DME	88% inversion	»
»	s-C_4H_9I	DME	71% inversion	»
Ph_3PbNa	s-C_4H_9Br	NH_3(liq.)	67.5% inversion	»
$(CH_3)_3SnNa$	*syn*-7-bromonorborn-2-ene	NH_3(liq.)	inversion	137
»	*anti*-7-bromonorborn-2-ene	»	*syn-anti* + tricycl. mixture	»
$(CH_3)_3SnLi$		THF	retention	139
»		»	inversion	»
»		»	retention	»
»		»	»	»
»		»	»	»
$(CH_3)_3SnLi$	*syn*-7-bromonorbornene	THF	84% inversion	140
»	»	DME	97% inversion	»
»	»	THF–TG	»	»
$(CH_3)_3SnNa$	»	THF	10% inversion (90% retention)	»
»	»	DME	81% inversion	»
»	»	THF–TG	91% inversion	»
$(CH_3)_3SnK$	»	THF	47% inversion	»
»	»	DME	18% inversion	»
»	»	THF–TG	96% inversion	»
$(CH_3)_3Sn(Li, Na, K)$	*anti*-7-bromonorbornene	THF, DME, THF–TG	79–99% retention	»
$(CH_3)_3SnLi$	1-bromomethyl-2,2-diphenylcyclopropane	THF	retention	138

Jensen and Davis[136] observed the preferential inversion of configuration in the reactions of Ph_3EM (E = Si, Ge, Sn, or Pb) with optically active s-butyl halides (Hal = Cl, Pr, or I), the extent of inversion of configuration increasing from the iodide to the chloride. In conformity with the study of Dessy et al.,[126] the authors treat their results as a consequence of an S_N2 process. However, as already pointed out in the discussion of the stereochemistry of the Wurtz reaction, the S_N2 mechanism explains only the inversion of configuration; in order to

‡ The triphenylmethyl dimer[132] having the structure



is probably meant.

account for the observed partial racemisation (Table 6), one must invoke another mechanism or the parallel occurrence of an exchange process and the loss of configuration in the organometallic compound RM formed. An inversion of configuration has also been observed in the reaction of trimethylstannylsodium with *syn*-7-bromonorborn-2-ene in liquid ammonia, but the analogous reaction with the *anti*-isomer led to the formation of a mixture of *syn*- and *anti*-isomers[127]. The reaction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane with Me_3SnLi takes place with retention of configuration[138].

The problem of the mechanisms of the reactions of organobimetallic compounds with R'X has been examined by Traylor et al.,[139] who investigated the stereochemistry of the reactions of trimethylstannyl-lithium with a series of halogeno-derivatives of cyclohexane, bi- and tri-cyclic compounds, and 4-t-butylcyclohexyltoluene-*p*-sulphonate (Table 6). The authors believe that the inversion of configuration is always a consequence of a reaction of the S_N2 type at the carbon atom. On the other hand, the observed retention of configuration can be accounted for on the basis of two mechanisms according to their view.

1. The metal–halogen exchange process, which the authors regard as an S_N2 reaction involving the halogen atom followed by a rapid Wurtz reaction:

$$R'Br + R_3SnLi \xrightarrow{\text{slow}} R'Li + R_3SnBr; \text{ (retention of configuration).}$$
$$R_3SnBr + R'Li \xrightarrow{\text{fast}} R_3SnR' + LiBr.$$

The authors suggest that the first stage proceeds with retention of configuration and the second stage probably also takes place with retention of configuration as a process of the S_E2 type involving the carbon atom. Furthermore, the RLi formed in the reaction are not racemised, probably owing to the structure of the R group.

2. A mechanism involving the SET stage:

$$R'Br + R_3Sn^- \rightarrow [R'^{\cdot}Br^- \ {}^{\cdot}SnR_3] \rightarrow R'SnR_3 + \text{olefin.}$$

Both mechanisms also explain the formation of distannane observed in the reaction, but the authors give preference to the former on the grounds that the geometrical configuration is retained in the reaction with *cis*-4-t-butylcyclohexyl bromide, while under conditions allowing rotation in the radical-ion pair the R_3Sn^- group should have occupied the more stable equatorial position.

To a significant degree, the stereochemistry of processes of this kind can depend on the nature of the solvent and the atom of the metal M. The results obtained by Kuivila et al. for the reactions of the *syn*- and *anti*-isomers of 7-bromonorbornenes with Me_3SnM in a series of ethereal solvents[140] are presented below.

Isomer	M	Retention of configuration, % THF	DME	THF–TG
syn-	Li	16	3	3
	Na	90	18	9
	K	3	92	4
anti-	Li	96	98	96
	Na	85	93	99
	K	79	92	96

The authors regard the results obtained as confirmation of the view that the "freer" ion pairs react preferentially with inversion of configuration. Indeed, in the case of the *syn*-isomer the highest percentage inversion is observed in the THF-tetraglyme (TG mixture) and for the lithium derivatives, which are most highly solvated, in all the solvents. A particularly marked solvent effect has been observed in the reaction with Me_3SnNa, where the stereochemical result varies from 70% retention in THF to 91% inversion in the THF–TG mixture. However, incomprehensible results have been obtained for the *anti*-isomer—the reaction proceeds in all solvents with almost complete retention of configuration. The reactions of 1- and 2-bromoadamantanes with Me_3SnM also involve a complete retention of configuration[140]. Analysis of the possible reaction mechanisms led the authors to the conclusion that the retention of configuration can be most simply explained by a four-centre transition state, although the alternative two-stage process and the mechanism including an SET stage (Traylor's mechanisms 1 and 2[139]) are not ruled out. We may note that, in the Wurtz reaction between RM and optically active alkyl halides, the retention of configuration in the product RR' has not been observed with the exception of the reactions of RM with vinyl halides, which take place with retention of geometrical configuration.

Finally, Eaborn and coworkers[141,142] studied the stereochemistry of the reactions of optically active ethylphenyl(α-naphthyl)germyl-lithium with a series of alkyl halides in ether and showed that the stereochemical result depends significantly on the nature of the halogen. Thus the reactions with chlorides and bromides took place predominantly with retention of the configuration at the germanium atom, while inversion of configuration was observed in the reactions with iodides. The configuration was retained also in the reaction with benzyl bromide. The authors explained the retention of configuration in this reaction by a four-centre transition state (I):

$$R_3\overset{*}{G}eLi + R'Hal \rightarrow \left[\begin{array}{c} R_3\overset{*}{G}e\cdots\cdots Li \\ \vdots \qquad\quad \vdots \\ R'\cdots\cdots Hal\ (Cl,\ Br) \end{array}\right] \rightarrow R_3\overset{*}{G}eR' + LiHal.$$
(I)

On the other hand, they believe that in reactions with iodides the exchange process (II) takes place initially and is followed by the Wurtz reaction between R_3GeI and R'Li, which results in inversion of configuration, as shown by the same investigators[143]:

$$R_3\overset{*}{G}eLi + R''I \rightarrow \left[\begin{array}{c} R_3\overset{*}{G}e\cdots\cdots Li \\ \vdots \qquad\quad \vdots \\ I\cdots\cdots R' \end{array}\right] \rightarrow R_3\overset{*}{G}eI + R'Li;$$
(II)
$$R_3\overset{*}{G}eI + R'Li \xrightarrow{\text{inversion}} R_3GeR' + LiI.$$

Thus analysis of the stereochemical data for the reactions of organobimetallic derivatives with R'X shows that the results cannot be accounted for by a single mechanism (as already stated, a similar situation was observed also for the reactions of RM with R'X).

XI. THE INTERACTION OF ORGANOMETALLIC COMPOUNDS WITH 'ONIUM SALTS

A radical mechanism has been proposed for the reactions of iodonium salts with Grignard reagents by Gragerov and coworkers[144] on the basis of the detection of triphenylmethyl radicals in the reactions of diphenyliodonium salts (X = BF_4, Cl, or I) with triphenylmethylmagnesium chloride and the detection of methane and ethane (5%) in the reaction of $Ph_2I^+BF_4^-$ with methylmagnesium iodide:

$$Ph_2I^+X^- + RMgX' \rightarrow Ph_2I^{\cdot} + R^{\cdot} + MgXX'.$$

However, the problem of whether the radical pathway is unique or whether it represents a side reaction, which becomes dominant for R = Ph_3C, remains unsolved.

A similar mechanism has been suggested also for reactions of t-butyl- and benzyl-magnesium chlorides with *p*-chlorophenyldiazonium fluoroborate in THF.[145] PhCl (40%), p-$ClC_6H_4N = NCMe_3$ (15,6%), isobutane (18%), isobutene (14%), and tetramethylbutane (77%) were detected in the former reaction. Furthermore, the polarisation of the vinyl protons of isobutene and of the methyl protons of isobutane was observed. The formation of chlorobenzene, toluene, and bibenzyl was noted in the reaction with benzylmagnesium chloride; chlorobenzene proved to be polarised. A study was also made of the interaction of diphenyliodonium bromide with methyl-, ethyl-, and phenyl-magnesium iodides and phenyl-lithium, toluene (59%), ethylbenzene (37%), and biphenyl (33 and 64% respectively) being observed. The authors were not particularly concerned with the study of the reaction mechanism, but they believe that the reaction is a process of the S_N2 type.[146]

The reaction of diphenyliodonium fluoroborate with α-bromomercuriphenylethyl acetate, which leads to the formation of a mixture of ethyl esters of phenylacetic, diphenylacetic, and 1,2-diphenylsuccinic acids, can only be treated from the standpoint of the SET mechanism[147]:

$$Ph_2IBF_4 + PhCH(HgBr)CO_2Et \rightarrow PhCH_2CO_2Et + Ph_2CHCO_2Et + (PhCHCO_2Et)_2.$$

Within the framework of the SET mechanism, an attempt could probably be made to treat the interaction of organolithium compounds with the sulphonium salts $Ph_3S^*BF_4^-$.[148-150] However, the experiments carried out using phenyl-lithium labelled with ^{14}C showed that, for the 1 : 1 reactant ratio, the isotopic label is distributed in equal amounts between the reaction products Ph_2 and Ph_2S, which agrees with the mechanism involving their formation from the intermediate sulphurane Ph_3Ph^+S, but can also be accounted for within the framework of the SET mechanism or on the assumption of the intermediate formation of dehydrobenzene[149]. Furthermore, the existence in solution at a low temperature (−78°C) of tetrakis(pentafluorophenyl)sulphurane, which decomposes on raising the temperature (−20° and 0°C) with formation of the corresponding fluorinated analogues of biphenyl and diphenyl sulphide, has been demonstrated. On the other hand, the addition of styrene or norbornene has no influence on the course of the reaction[150].

It is apparently of interest to investigate the reactions of organomagnesium compounds with sulphenyl chloride[151,152] for which an electron transfer stage may be postulated in certain cases, bearing in mind that sulphenyl halides are reduced much more readily than alkyl or aryl halides[153,154]:

$$ArSCl\ (AlkSCl) + Ar'MgX \rightarrow ArSAr'\ (AlkSAr') + MgXCl.$$

Unfortunately, a complete analysis of the products was not carried out in the above investigations[151,152] and only the yields of the corresponding sulphides are indicated (55–70%), which does not allow one to infer that radical stages occur in the reaction.

REFERENCES

1. E. Späth, Monatsh., **34**, 1965 (1913).
2. R. Abegg, Ber., **38**, 4110 (1905).
3. M. L. Bert, Compt. rend., **186**, 587 (1928).
4. J. Houben, Ber., **36**, 3083 (1903).
5. R. L. Letsinger, J. Amer. Chem. Soc., **70**, 406 (1948).
6. R. L. Letsinger and J. G. Traynham, J. Amer. Chem. Soc., **72**, 849 (1950).
7. L. H. Sommer and W. D. Korte, J. Org. Chem., **35**, 22 (1970).
8. W. D. Korte and J. Kenner, Tetrahedron Letters, 603 (1970).
9. S. Sauer and W. Braig, Tetrahedron Letters, 4275 (1969).
10. M. Gomberg and P. Kahn, J. Amer. Chem. Soc., **39**, 2009 (1917).
11. J. Schmidlin, Ber., **43**, 1137, 1141 (1900).
12. E. van Meyer, J. prakt. Chem., **82**, 521 (1910).
13. K. Ziegler and E. Boeye, Annalen, **458**, 253 (1927).
14. K. Ziegler and C. Ochs, Ber., **55**, 2257 (1922).
15. H. Gilman and H. L. Jones, J. Amer. Chem. Soc., **51**, 2840 (1929).
16. M. Gomberg and L. H. Cone, Ber., **39**, 1461, 2957 (1906).
17. J. Schmidlin and P. Massini, Ber., **42**, 2384 (1909).
18. R. C. Fuson, J. Amer. Chem. Soc., **48**, 830 (1926).
19. R. C. Fuson, J. Amer. Chem. Soc., **48**, 2681 (1926).
20. H. Gilman and J. E. Kirby, J. Amer. Chem. Soc., **48**, 1733 (1926).
21. M. S. Kharash and P. Reinmuth, "Grignard Reaction of Nonmetallic Substances", Prentice-Hall, New York, 1954.
22. R. G. Gough and J. A. Dixon, J. Org. Chem., **33**, 2148 (1968).
23. M. M. Aleksankin, B. V. Chizhov, I. V. Gol'denfel'd, and I. P. Gragerov, Zhur. Org. Khim., **1**, 1909 (1965).
24. P. R. Singh, S. R. Tayal, and A. Nigam, J. Organometal. Chem., **42**, C9 (1972).
25. H. R. Ward, R. G. Lawler, and T. A. Marzilli, Tetrahedron Letters, 521 (1970).
26. L. F. Kasukhin, M. P. Ponomarchuk, and Zh. F. Buteiko, Zhur. Org. Khim., **8**, 665 (1972).
27. L. S. Degtyarev, M. P. Ponomarchuk, and L. F. Kasukhin, Zhur. Org. Khim., **8**, 2353 (1972).
28. E. Osawa, Z. Majerski, and P. R. von Schleyer, J. Org. Chem., **36**, 205 (1971).
29. D. Seyferth and B. Prokai, J. Org. Chem., **31**, 1702 (1966).
30. W. Reeve, R. Brown, and T. F. Steckel, J. Amer. Chem. Soc., **93**, 4607 (1971).
31. K. D. Berlin, R. D. Shupe, and R. D. Grigsby, J. Org. Chem., **34**, 2500 (1969).
32. C. S. Marvell, F. D. Hager, and D. D. Coffman, J. Amer. Chem. Soc., **49**, 2323 (1927).
33. A. A. Morton, J. B. Davidson, and B. L. Hakan, J. Amer. Chem. Soc., **64**, 2242 (1942).
34. E. Le Goff, S. E. Ulrich, and D. B. Denner, J. Amer. Chem. Soc., **80**, 622 (1958).
35. N. G. Brink, J. F. Lane, and E. S. Wallis, J. Amer. Chem. Soc., **65**, 943 (1943).
36. R. L. Letsinger, Angew. Chem., **70**, 151 (1958).
37. J. F. Lane and S. E. Ulrich, J. Amer. Chem. Soc., **75**, 3975 (1953).
38. J. F. Eastham and G. W. Gibson, J. Amer. Chem. Soc., **85**, 2171 (1963).
39. J. F. Eastham and G. W. Gibson, J. Org. Chem., **28**, 280 (1963).
40. I. B. Peletskaya, S. V. Rykov, V. B. Vol'eva, A. L. Buchachenko, and N. V. Kessenikh, Izv. Akad. Nauk SSSR, Ser. Khim., 685 (1972).
41. C. W. Jefford, D. Kirkpatrick, and F. Delay, J. Amer. Chem. Soc., **94**, 8905 (1972).
42. D. Bryce-Smith, J. Chem. Soc., 1603 (1956).
43. S. A. Kandil and R. E. Dessy, J. Org. Chem., **30**, 3857 (1965); J. Amer. Chem. Soc., **88**, 3027 (1966).
44. H. R. Ward, J. Amer. Chem. Soc., **89**, 5517 (1967).

45. F. S. D'yachkovskii, N. N. Bubnov, and A. E. Shilov, Dokl. Akad. Nauk SSSR, **123**, 870 (1958).
46. H. R. Ward, Ind. Chim. belge, **36**, 1085 (1971).
47. F. S. D'yachkovskii and A. E. Shilov, Zhur. Obshch. Khim., **33**, 406 (1963).
48. D. E. Applequist and D. F. O'Brien, J. Amer. Chem. Soc., **85**, 743 (1963).
49. D. J. Cram, "Fundamentals of the Chemistry of Carbanions" (Translated into Russian), Izd. Mir, Moscow, 1967.
50. G. Wittig, Bull. Soc. chim. France, 1352 (1963).
51. H. J. S. Winkler and H. Winkler, J. Amer. Chem. Soc., **88**, 964, 969 (1966).
52. H. R. Ward and R. G. Lawler, J. Amer. Chem. Soc., **89**, 5518 (1967).
53. H. R. Ward, R. G. Lawler, and R. A. Cooper, J. Amer. Chem. Soc., **91**, 746 (1969).
54. A. R. Lepley and R. L. Landay, J. Amer. Chem. Soc., **91**, 748 (1969).
55. K. A. Bilevich and O. Yu. Okhlobystin, Uspekhi Khim., **37**, 2162 (1968) [Russ. Chem. Rev., No. 12 (1968)].
56. J. Rakshys, Chem. Comm., 578 (1970).
57. T. V. Leshina, R. Z. Gardeev, M. A. Kamka, S. M. Shein, and Yu. N. Molin, Zhur. Org. Khim., **8**, 2366 (1972).
58. H. R. Ward, R. G. Lawler, and H. I. Lokek, Zhur. Org. Khim., **90**, 7359 (1968).
59. H. R. Ward, R. G. Lawler, H. I. Lokek, and R. A. Cooper, Zhur. Org. Khim., **91**, 4928 (1971).
60. J. F. Garst and R. H. Cox, J. Amer. Chem. Soc., **92**, 6389 (1970).
61. G. A. Russell and D. W. Lampson, J. Amer. Chem. Soc., **91**, 3967 (1969).
62. F. W. Evans and M. Szwarz, Trans. Faraday Soc., **57**, 1905 (1961).
63. D. F. Hoeg and D. L. Lusk, J. Organometal. Chem., **5**, 1 (1966).
64. R. Palland and J. M. Plean, Compt. rend., **C267**, 507 (1968).
65. R. E. Merrill and Ei-ichi Negishi, J. Org. Chem., **39**, 3452 (1974).
66. L. J. Zakharkin, O. Y. Oklobystin, and B. N. Strunin, J. Organometal. Chem., **4**, 349 (1965).
67. L. J. Zakharkin, O. Y. Oklobystin, and K. A. Bilevich, J. Organometal. Chem., **2**, 309 (1964).
68. H. S. Kharasch and W. H. Urry, J. Org. Chem., **13**, 101 (1948).
69. R. L. Letsinger, J. Amer. Chem. Soc., **72**, 4842 (1950).
70. G. Wittig, Chem. Ber., **83**, 359 (1950).
71. W. H. Glase, C. M. Seldom, A. L. Ball, and L. E. Bray, J. Org. Chem., **34**, 641 (1969).
72. D. J. Curtin and E. E. Harris, J. Amer. Chem. Soc., **73**, 2716 (1951).
73. D. J. Curtin and E. E. Harris, J. Amer. Chem. Soc., **73**, 4519 (1951).
74. A. N. Nesmeyanov, A. E. Borisov, and N. A. Vol'kenau, Izv. Akad. Nauk SSSR, Ser. Khim., 992 (1954).
75. M. J. S. Dewar and J. M. Harris, J. Amer. Chem. Soc., **91**, 3653 (1969).
76. H. M. Walborsky, F. J. Impastato, and A. E. Young, J. Amer. Chem. Soc., **86**, 3283 (1964).
77. S. E. Ulrich, F. H. Gentes, J. F. Lane, and E. S. Walles, J. Amer. Chem. Soc., **72**, 5127 (1950).
78. E. Bergman, Helv. Chim. Acta, **20**, 590 (1937).
79. R. L. Burwell, A. D. Schields, and H. Hart, J. Amer. Chem. Soc., **76**, 908 (1954).
80. H. Zook and R. N. Goldey, J. Amer. Chem. Soc., **75**, 3976 (1953).
81. G. Whitesides, W. F. Fischer, J. San Filipo, R. W. Bashe, and H. O. House, J. Amer. Chem. Soc., **91**, 4871 (1969).
82. E. J. Corey and G. H. Posner, J. Amer. Chem. Soc., **89**, 3911 (1967).
83. E. J. Levene and R. E. Marker, J. Biol. Chem., **97**, 563 (1952).
84. E. Ott, Ber., **61**, 2124 (1928).
85. P. Skell and G. Bean, J. Amer. Chem. Soc., **84**, 4660 (1962).
86. K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions" (Translated into Russian), Izd. Mir, Moscow, 1971.
87. I. P. Beletskaya, V. B. Vol'eva, and O. A. Reutov, Dokl. Akad. Nauk SSSR, **195**, 360 (1970).
88. I. P. Beletskaya, V. B. Vol'eva, S. V. Rykov, A. L. Buchachenko, and A. V. Kessennikh, Izv. Akad. Nauk SSSR, Ser. Khim., 454 (1971).
89. S. Bank and D. A. Noyd, J. Amer. Chem. Soc., **95**, 8203 (1973).
90. O. A. Reutov, E. V. Uglova, and V. D. Makhaev, Dokl. Akad. Nauk SSSR, **188**, 833 (1969).
91. A. A. Reutov, E. V. Uglova, V. D. Makhaev, and V. S. Petrosyan, Zhur. Org. Khim., **6**, 2153 (1970).
92. E. V. Uglova, V. D. Makhaev, and O. A. Reutov, Zhur. Org. Khim., **6**, 1337 (1970).
93. I. P. Beletskaya, S. V. Rykov, V. B. Vol'eva, A. L. Buchachenko, and A. V. Kessennikh, Izv. Akad. Nauk SSSR, Ser. Khim., 685 (1972).
94. S. F. Zhil'tsov, Zhur. Obshch. Khim., **43**, 586 (1973).
95. K. A. Bilevithch, N. N. Bubnov, O. Y. Oxhlobystin, Tetrahedron Letters, 3465 (1968).
96. P. R. Jones and S. J. Constanzo, J. Org. Chem., **38**, 3189 (1973).
97. P. W. N. M. Van Leeuwen, R. Kaptein, R. Huis, and W. J. Kalisvaart, J. Organometal Chem., **93**, C5 (1975).
98. J. F. Normant, Synthesis, **2**, 6380 (1972).
99. N. Nilson and O. Wennerstrom, Tetrahedron Letters, 3307 (1968).
100. C. R. Johnson and G. A. Dutra, J. Amer. Chem. Soc., **95**, 7777, 7783 (1973).
101. A. A. Moroz and M. S. Shvartsberg, Uspekhi Khim., **43**, 1443 (1974) [Russ. Chem. Rev., No. 8 (1974)].
102. G. W. Parshell and J. J. Mrowca, Adv. Organometal. Chem., **7**, 157 (1968).
103. J. Halpern, Accounts Chem. Res., **3**, 386 (1970).
104. J. L. Peterson, T. E. Nappier, and D. W. Meek, J. Amer. Chem. Soc., **93**, 8195 (1973).
105. D. Strope and D. F. Shriver, J. Amer. Chem. Soc., **93**, 8197 (1973).
106. J. Chatt and B. L. Shaw, J. Chem. Soc., 705 (1959).
107. C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, Inorg. Chem., **2**, 1255 (1963).
108. T. G. Appleton, H. C. Clark, and L. E. Manzen, J. Organometal. Chem., **65**, 275 (1974).
109. A. Tamaki and J. K. Kochi, J. Organometal. Chem., **40**, C81 (1972).
110. A. Tamaki and J. K. Kochi, J. Organometal. Chem., **51**, C39 (1973).
111. A. Tamaki and J. K. Kochi, J. Organometal. Chem., **64**, 411 (1974).
112. J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, J. Amer. Chem. Soc., **94**, 4043 (1972).

113. R. G. Pearson and W. R. Muer, J. Amer. Chem. Soc., 92, 5519 (1970).
114. J. A. Labinger, A. V. Kramer, and J. A. Osborn, J. Amer. Chem. Soc., 95, 7908 (1973).
115. R. S. Wade and C. E. Castro, J. Amer. Chem. Soc., 95, 226 (1973).
116. R. S. Wade and C. E. Castro, J. Amer. Chem. Soc., 95, 231 (1973).
117. J. Halpern and J. P. Maher, J. Amer. Chem. Soc., 87, 5361 (1965).
118. J. Kwiatek and J. K. Seyler, J. Organometal. Chem., 3, 421 (1965).
119. K. Kochi and D. D. Davis, J. Amer. Chem. Soc., 86, 5264 (1964).
120. P. W. Schneider, P. F. Phelan, and J. Halpern, J. Amer. Chem. Soc., 91, 77 (1969).
121. G. N. Schrauzer, Accounts Chem. Res., 1, 97 (1968).
122. G. N. Schrauzer and R. J. Windgassen, J. Amer. Chem. Soc., 88, 3738 (1966).
123. G. N. Schrauzer, E. Deutsch, and R. J. Windgassen, J. Amer. Chem. Soc., 90, 2441 (1968).
124. G. N. Schrauzer and E. Deutsch, J. Amer. Chem. Soc., 91, 3341 (1969).
125. F. R. Jensen, V. Madan, and D. H. Buchanan, J. Amer. Chem. Soc., 92, 1414 (1970).
126. R. E. Dessy, R. L. Pole, and R. B. King, J. Amer. Chem. Soc., 88, 5121 (1966).
127. N. S. Vyazankin, V. T. Bychkov, O. N. Linzina, L. V. Alexandrova, and H. G. A. Rusuvaev, J. Organometal. Chem., 31, 311 (1971).
128. H. Sakura, A. Okada, M. Kira, and K. Jonezawa, Tetrahedron Letters, 1511 (1971).
129. V. T. Bychkov, N. S. Vyazankin, G. A. Abakumov, O. V. Linzina, and G. A. Razuvaev, Dokl. Akad. Nauk SSSR, 202, 593 (1972).
130. N. S. Vyazankin, G. A. Razuvaev, and E. I. Gladyshev, Dokl. Akad. Nauk SSSR, 151, 1326 (1963).
131. N. S. Vyazankin, G. A. Razuvaev, and E. I. Gladyshev, Dokl. Akad. Nauk SSSR, 155, 830 (1964).
132. H. Lunkamp, W. T. Nauta, and C. MacLean, Tetrahedron Letters, 249 (1968).
133. R. Fields, R. N. Haszeldine, and R. E. Hutton, J. Chem. Soc., 1967 C, 2559.
134. R. M. G. Roberts, J. Organometal. Chem., 63, 159 (1973).
135. D. J. Pasto and P. W. Wojtkowski, J. Organometal. Chem., 34, 251 (1972).
136. F. R. Jensen and D. D. Davis, J. Amer. Chem. Soc., 93, 4047 (1971).
137. C. H. W. Jones, R. G. Jones, P. Partington, and R. H. G. Roberts, J. Organometal. Chem., 32, 201 (1971).
138. K. Sisido, S. Kozima, and K. Takizama, Tetrahedron Letters, 33 (1967).
139. G. S. Koermer, M. L. Hall, and T. G. Traylor, J. Amer. Chem. Soc., 94, 7205 (1972).
140. H. G. Kuivila, J. L. Considene, and J. D. Kennedy, J. Amer. Chem. Soc., 94, 7209 (1972).
141. C. Eaborn, R. E. Hill, and P. Simpson, J. Organometal. Chem., 15, P1 (1968).
142. C. Eaborn, R. E. Hill, and P. Simpson, J. Organometal. Chem., 37, 275 (1972).
143. C. Eaborn, R. E. Hill, and P. Simpson, J. Organometal. Chem., 37, 251 (1972).
144. A. S. Levit, N. N. Kalibabchuk, and I. P. Gragerov, Dokl. Akad. Nauk SSSR, 199, 1325 (1971).
145. V. J. Savin, J. D. Temyachev, and Y. P. Kitaev, Org. Magn. Reson., 5, 449 (1973).
146. F. M. Beringer, A. Brierley, M. Drexlev, E. M. Gindlev, and C. C. Lumpkin, J. Amer. Chem. Soc., 75, 2708 (1953).
147. A. N. Nesmeyanov, L. G. Makarova, and V. N. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 1966 (1969).
148. A. W. LaRochelle and F. M. Trost, J. Amer. Chem. Soc., 93, 6077 (1971).
149. D. Harrington, J. Weston, J. Jacobus, and K. Mislow, Chem. Comm., 1079 (1972).
150. W. A. Sheppard, J. Amer. Chem. Soc., 93, 5597 (1971).
151. F. Holschneider, K. Köberle, W. Speer, P. Stocklin, and H. Lecher, Ber., 68, 409 (1924).
152. H. Brintzinger and H. Schmahl, Ber., 87, 314 (1954).
153. P. Zuman, in "Progress in Physical Organic Chemistry", Interscience Publ., 1967, Vol. V, p. 81.
154. M. I. Kalinkin, N. T. Ioffe, and K. P. Butin, Izv. Akad. Nauk SSSR, Ser. Khim., 2072 (1969).
155. R. B. Allen, R. G. Lawler, and H. R. Ward, Tetrahedron Letters, 3303 (1973).
156. J. P. Mapes, D. E. Gregory, and K. D. Berlin, Proc. Okla. Acad. Sci., 53, 70 (1972); Chem. Abs., 77, 151220P (1972).

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