Journal of Organometallic Chemistry, 100 (1975) 219—235

THE MECHANISMS OF THE SUBSTITUTION REACTIONS OF NON-TRANSITION METAL ORGANOMETALLIC COMPOUNDS

O.A. REUTOV

Department of Chemistry, Moscow State University, Moscow (U.S.S.R.)

S_E2 reactions

As a result of kinetical and stereochemical studies of electrophilic substitutions at saturated carbon atoms (reactions of types 1-5) the conclusion has been

$$2\ \mathrm{RHgX} \overset{\mathrm{N}}{\rightarrow} \mathrm{R_2Hg} + \mathrm{N \cdot HgX_2} \qquad [5\text{-}14] \qquad (1)$$

$$\mathrm{R_2Hg} + \mathrm{HgX_2} \rightarrow 2\ \mathrm{RHgX} \qquad [15\text{-}21] \qquad (2)$$

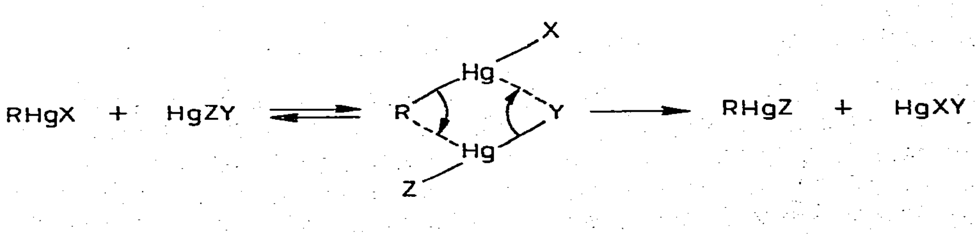
$$\mathrm{RHgX} + \overset{*}{\mathrm{Hg}}\mathrm{X_2} \rightleftharpoons \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{HgX_2} \qquad [22\text{-}43] \qquad (3)$$

$$\mathrm{RHgX} + \mathrm{R'}\overset{*}{\mathrm{Hg}}\mathrm{X} \rightleftharpoons \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} + \mathrm{R'HgX} \qquad [44] \qquad (4)$$

$$\mathrm{R_2Hg} + \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{X} \rightleftharpoons \mathrm{R_2}\overset{*}{\mathrm{Hg}} + \mathrm{RHgX} \qquad [45\text{-}47] \qquad (5)$$

$$[\overset{*}{\mathrm{Hg}} = {}^{203}\mathrm{Hg}]$$

drawn that in solvents of low polarity the closed transition state (A) is involved (S_Ei reactions):



(A)

Even in polar solvents the substitution proceeds via a closed transition state of the type A under conditions of anionic catalysis, e.g. in the S_E2 reactions of

---

* See refs. 1-4 for reviews.

isotopic exchange between benzylmercury bromides and $HgBr_2$ in quinoline or DMSO in the presence of KBr [40, see also 34].

The S_E2 reactions at saturated carbon atoms occur with retention of stereochemical configuration*. (S_E2 rule) [9,16,32-36]. The S_E2 rule has a general applicability, and applies not only to closed transition states (S_Ei) but also to open transition states.

S_E1(N) reactions**

S_E1 reactions known at present proceed via a mechanism in which the rate-determining step involves attack on the substrate by some nucleophile present in solution, the reaction with the electrophilic agent occurring as a fast step. If the system shows no appropriate nucleophilic catalyst, the reaction usually does not occur or it follows an S_E2 mechanism (when the nucleophilicity of the group R and the electrophilicity of the attacking agent are sufficiently high). Unimolecular electrophilic substitution processes should therefore be classified as S_E1(N) reactions. It is assumed that attack by the nucleophile causes ionization of the C—m bond, which is followed by a rapid shift of the equilibrium under the influence of the electrophilic agent:

$$R{-}m + N \underset{k_{-1}}{\overset{k_1,\,\text{slow}}{\rightleftharpoons}} [R^{\delta-} \ldots m^{\delta+} \ldots N] \rightleftharpoons \underset{\text{ion pair}}{R^-\ mN^+} \xrightarrow[E^+]{k_2,\,\text{fast}} RE + [mN]^+$$

(rate $= k_1[\mathrm{Rm}][\mathrm{N}]$, if $k_2 \gg k_{-1}$; N = nucleophile, m— = a metal bond)

The function of the nucleophile N may be discharged by anions or neutral molecules, e.g. solvent molecules, capable of coordinating to the metal atom in the organometallic compound. Furthermore, the reactions may occur under conditions in which the role of the nucleophilic catalyst is played by the nucleophilic part N of an electrophilic agent EN. In this case the choice between an S_E1 and $S_E2(S_Ei)$ mechanism is very difficult, since a kinetic order of 2 would apply in both cases.

The first evidence for S_E1 mechanism came from the study of mercury-isotope exchange of ethyl α-bromomercuryphenylacetate with $^{203}HgBr_2$ in DMSO [30,31]:

$$PhCH(HgBr)COOEt + \overset{*}{H}gBr_2 \overset{DMSO}{\rightleftharpoons} PhCH(\overset{*}{H}gBr)COOEt + HgBr_2$$

The reaction is of first order in the organomercury compound and zero order in mercury bromide. The first step involves ionization of the organomercury compound, such ionization being facilitated by aprotic dipolar solvents such as DMSO; in the second step the ion pair so generated reacts rapidly with an electrophile ($\overset{*}{H}gBr_2$). The degree of ionization in the transition state is apparently influenced by the strength of the nucleophile and the stability of

---

* One interesting exception to the S_E2 rule is the configuration inversion in the reaction of butyltrisneopentyltin with bromine [48]. The main reason for such behaviour appears to be the steric hindrance in this reaction.

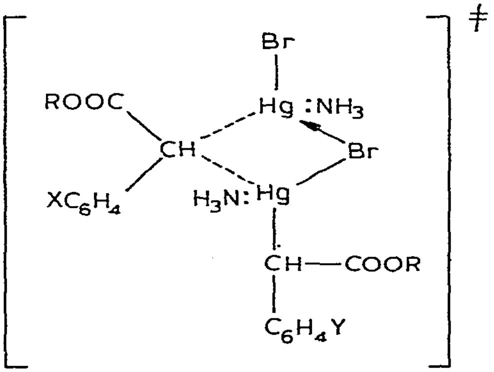
** See ref. 49 for a review.

the carbanion in the ion pair. The relatively stable anion of phenylacetic ester ($pK_a \sim 17$) becomes planar, and as a result racemization occurs [37].

Studies of the symmetrization reaction of substituted ethyl α-bromomercuryphenylacetates with ammonia in chloroform showed that the reaction was second order in the organomercury compound and also second order in ammonia [8], however the observed effect of substituents $NO_2 > Hal > H > alkyl$ ($\rho = 2.8$) did not agree with the designation of the reaction as S_E2 [13].

$$2XC_6H_4CH(HgBr)COOEt \xrightarrow[(CHCl_3)]{NH_3} (XC_6H_4CHCOOEt)_2Hg + HgBr_2 \cdot (NH_3)_2$$

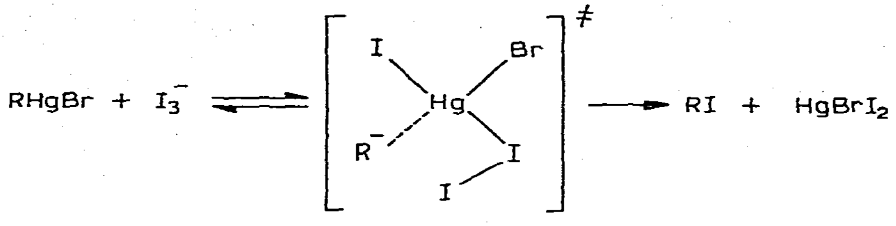
Earlier this reaction had been assigned to the S_Ei class. It was assumed that the reaction proceeded through a four-center type transition state in which the original C—Hg bond cleaves before the new C—Hg bond is formed. It was found also that when the substituents, X and Y, had opposite polar effects the reaction rate increased ("cosymmetrization effect"), and in the transition state the molecules are arranged in such a way so as to facilitate both the coordination Br—Hg (Y is an electron-releasing substituent) and the cleavage of C—Hg bond (X is an electron-withdrawing substituent) [14]. All these facts can now be readily explained on the assumption that the correct reaction mechanism is $S_E1(N)$, with the second reagent molecule bearing a coordinated ammonia molecule behaving as a nucleophilic catalyst (or assistor) this behaviour being in line with the known coordination properties of mercury. The retention of stereochemical configuration in this $S_E1(N)$ type reaction arises from the necessary orientation of the reagents associated with the Br→Hg coordination.



S_E1 (N)

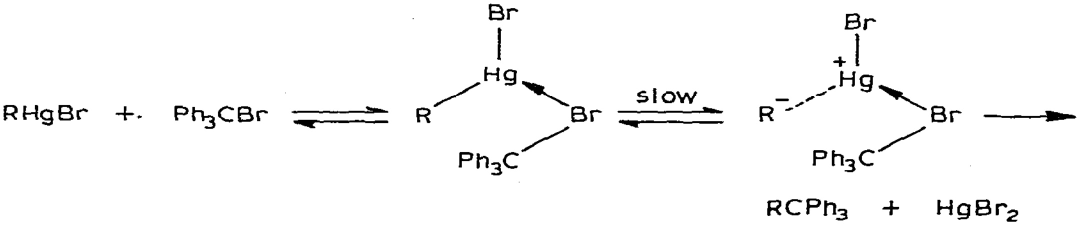
The observed formal second order kinetics and "abnormal" (in terms of S_E2 mechanism) substituent effects in reactions of ethyl α-bromomercuryphenylacetate with I_3^- [50], $\rho = 2.3$ may be explained in a similar fashion.

The I_3^- anion behaves not only as an iodinating agent in the reaction, but also as a nucleophilic catalyst [$S_E1(I_3^-)$ mechanism]. It is suggested that the complex, $RHgX \cdot I_3^-$, is formed initially in this reaction, and that further slow ionization occurs along the C—Hg bond; such a preequilibrium step is always involved when the solvent functions as a nucleophile.



(R = $XC_6H_4CHCOOEt$)

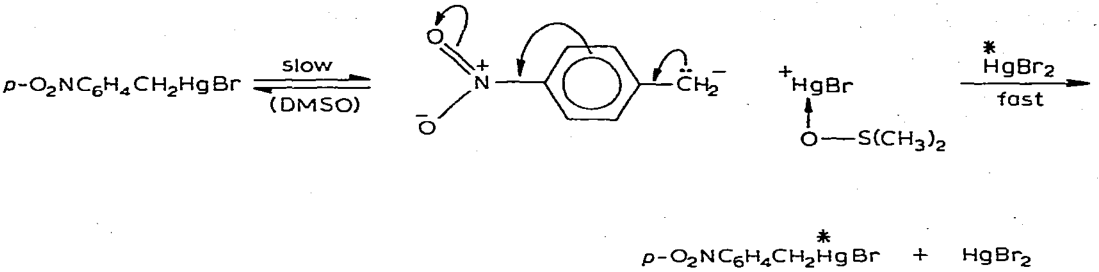
Probably the best illustrative example of such reactions is the reaction of ethyl α-bromomercuryphenylacetate with triphenylbromomethane. This reaction, which, depending on the nature of the solvent gives either C- or O-tritylation products [51], involves as a fast step of formation of the complex $RHgX \cdot Ph_3CBr$. This complex undergoes decomposition by a first order process, and the effect of substituents in phenyl group ($NO_2 > Hal > H >$ alkyl) is in accord with the assumption that C—Hg bond ionization is the rate limiting step [52]:



Thus, triphenylbromomethane acts not only as an electrophilic agent but also as a nucleophilic catalyst, and the reaction may be assigned an $S_E1(Ph_3CBr)$ mechanism.

It is noteworthy that when this reaction is carried out with the complex $Ph_3CBr \cdot HgBr_2$, second order kinetics are observed and the substituent effects agree with the S_E2 mechanism, i.e. alkyl > H > Hal > NO_2 (negative ρ). It is evident that even with the complex $Ph_3CBr \cdot HgBr_2$, some Br → Hg coordination takes place (i.e. S_Ei mechanism), since the stronger electrophilic agent, Ph_3CClO_4, which is incapable of nucleophilic assistance, is practically inactive in this reaction. It must thus be concluded that the weak coordination occurring in the reaction with the mercury bromide complex is insufficient to cause C—Hg bond ionization, but such coordination increases both the substrate nucleophilicity and the trityl bromide electrophilicity to an extent that is sufficient to allow the S_Ei reaction mechanism. This reaction provides an illustration of the fact that there are many kinds of reaction, which are intermediate between two extreme cases of "pure" S_E1 and S_E2 mechanisms and which, indeed, are of the most occurrence, and which differ one from the other only in the degree of carbon—metal bond ionization in the transition state.

Mercury isotopic exchange in some substituted benzylmercury bromides with $^{203}HgBr_2$ in quinoline and DMSO has been found to occur by the S_E2 mechanism [40,41]. The only exception is *p*-nitrobenzylmercury bromide, which reacts by the $S_E1(N)$ mechanism in DMSO [41].



Thus, introducing a *p*-nitro group (or α-carboethoxy group) into a molecule of benzylmercury bromide alters the reaction mechanism. Undoubtedly, the explanation for this behaviour lies in the fact that the electron-withdrawing substituent increases both the carbanion stability and the tendency of the metal to undergo nucleophilic attack.

An unusually strong nitro group effect has been observed in the reactions of a series of substituted benzylmercury chloride with I_3^- [54], which are second order. Substituent effects on the reaction rate are of the usual pattern for the S_E2 (or S_Ei) mechanism, viz. alkyl > H > Hal, but the nitro group is an exception. Under the reaction conditions, *p*-nitrobenzylmercury chloride reacts instantaneously, and it is reasonable to suppose that there is a change of mechanism in passing to the nitro compound.

Interesting data have been obtained from a study of the protolysis of a series of organomercury compounds, R_2Hg, by HCl in DMF as a solvent [49, p. 73]. The plot of Fig. 1 shows the dependence of the protolysis rate constants on the pK_a values of the corresponding carbon acids RH.

It is clear that the plot has two branches: in the case of stable carbanions the R_2Hg protolysis rate decreases with decreasing acidity of RH, whereas for unstable carbanions the rate increases with pK_a. These results can be explained if in the particular series of organomercury compounds investigated the $S_E1(N)$ mechanism is assumed to change to S_E2.

The S_E1 mechanism has been proposed for several other reactions [55-58].

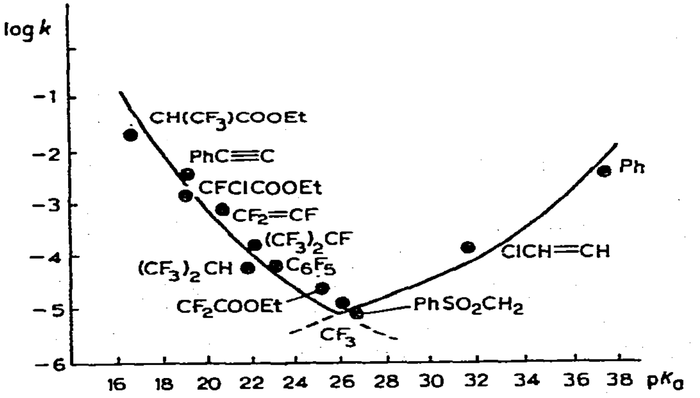


Fig. 1. Dependence of the protolysis rate constants on the pK_a values of the corresponding carbon acids, RH.

The following equilibrium in DMSO [59] may be formally regarded as involving S_E1 reactions:

$$\underset{\text{(I)}}{Ph_3\overset{+}{P}\text{—}CH(COR)HgCl} + Cl^- \rightleftharpoons \underset{\text{(II)}}{Ph_3\overset{+}{P}\text{—}\overset{-}{C}HCOR} + HgCl_2$$

In this case the ease of ionization of the C—Hg bond is associated with formation of the stable carbanionic center in the phosphorus ylid, II. The reactivity of compound I has been discussed in refs. 60-62.

The significance of pK_a values in organometallic chemistry*

σ-Organometallic compounds may be considered as metal salts of hydrocarbons, and therefore CH-acidity is of special importance in understanding organometallic reactivity.

One method for studying CH-acidity is based on experimental determination of parameters of polarographic reduction of organomercury compounds, R_2Hg[63—65]. For the estimation of CH-acidities the redox properties of organomercury compounds are used since the R_2Hg reduction potentials are very sensitive to changes in the organic group structure. The relation between pK_a values of CH-acids, RH, and electrochemical properties of the respective organomercury compounds, R_2Hg, is given by equation 1:

$$\Delta(\alpha n_a E_{1/2}) = \rho \times \Delta pK_a \qquad (1)$$

where ΔpK_a is the difference between pK_a's for a pair of CH-acids, $E_{1/2}$ the half-wave potential for R_2Hg, α the electrochemical transfer coefficient (which is, in a sense, analogous to the Brönsted coefficient) and n_a is the number of electrons in the potential-determining step.

This equation has been applied to a large series of organomercury compounds, and, as a result, the polarographic scale of CH-acidity was constructed [66,67]. This scale covers a more complex scale of pK_a's than any other in the literature: it involves CH-acids with pK's from 0 to 60, such as alkanes, arenes, alkenes [65], haloforms [68], carboranes [69,70], heterocyclic aromatics [71], etc. It has been shown that eqn. 1 applies not only to organomercury compounds but also to cobalt(III) and palladium(II) complexes [72]. The only parameter in eqn. 1 which is not accessible by theoretical calculation is the ρ constant. This constant must be estimated experimentally from some representative points.

pK_a values provide a quantitative measure of carbanion stabilities. In a number of cases one can predict the reactivity of an organometallic compound, R_nM, from the pK_a of RH. Thus organomercury compounds, R_2Hg, involving a group R which is capable of existence as a relatively stable carbanion, R^-, undergo hydrolysis in aqueous DMF in the presence of tetra-n-butylammonium iodide as catalyst; the hydrolysis rate increases with decreasing pK_a of RH by linear interrelation [73] ($\log k_1 = 0.17\ pK_a +$ const.). The linear interrelation between

---

* Figure 1 represents a good illustration of the significance of pK_a values for organometallic chemistry.

log k_1 and pK_a is one of the criteria for assignment of the reaction to S_E1-type [49].

Another example is the application of pK_a's to the prediction of the equilibrium constants of redistribution reactions involving a series of organomercury compounds [74]. The approach is to consider the R_2Hg compounds as complexes of carbanions, R_i^-, with cations, R_jHg^+. In such an approach the equilibrium constant for the "tetraalkyl" exchange 2 may be written as

$$K_p = \frac{K(R^1Hg, R^4) \cdot K(R^3Hg, R^2)}{K(R^1Hg, R^2) \cdot K(R^3Hg, R^4)}$$

$$R^1HgR^2 + R^3HgR^4 \rightleftharpoons R^1HgR^4 + R^2HgR^3 \tag{2}$$

where $K(R_jHg, R_i)$ is the affinity of carbanion R_i^- for cation R_jHg^+. If the affinities of carbanions for organomercury cations and for a proton are linearly dependent [75], one can write for the reaction of eqn. 2 the following expression:

$$\log K_p = (A^1 - A^3) \times \Delta pK_a(R^4H, R^2H) \tag{3}$$

where A^1 and A^3 are the slopes of plots in coordinates $\log K(RHg^+, R_i^-) - pK_a(R_iH)$ for the cations R^1Hg^+ and R^3Hg^+ respectively. Equation 3 applies well to most of the redistribution equilibria studied by us and other authors. The conclusion may be drawn that the thermodynamically preferred state of the system 2 is that in which both the mercury atoms differ least one from another. In other words, if pK_a values for carbanions increase in the order: $R^1 < R^2 < R^3 < R^4$, the equilibrium 2 will be shifted in such a way that the mercury atom will be bonded to the least and the most stable carbanions, R^1 and R^4, in one organomercury compound, and with carbanions of intermediate stabilities, R^2 and R^3, in another.

$$R^1HgR^2 + R^3HgR^4 \rightarrow R^1HgR^4 + R^2HgR^3 \leftarrow R^1HgR^3 + R^2HgR^4$$

The A values in eqn. 3 characterize the hardness (or softness) of organomercury cations relative to protons. As a rule, a harder cation, R_iHg^+, corresponds to a stronger acid, R_iH.

An analogous approach may probably be used to explain redistribution equilibria in other systems, e.g. in organometallic compounds of Group IVB of the Mendeleev Periodic system.

Nucleophilic catalysis in S_E reactions

The added complexing agent (anions or neutral molecules) can increase the rates of S_E reactions of organometallic compounds by several powers of ten. Use of nucleophilic catalysis may change the reaction mechanism; thus, it was shown that the reactions of RHgX with iodine or bromine proceed by a homolytic mechanism, but the mechanism changes to S_E2 in the presence of some anions or neutral nucleophiles [76].

In CCl_4 under anaerobic conditions, the reaction of RHgX (R = alkyl) with Br_2 results in the formation of racemic RBr. In the presence of air this reaction is strongly retarded, and there is partial (to 30%) retention of configuration. Reactions of RHgX with I_2 in DMF in the presence of CdI_2 and with Br_2 in methanol in the presence of NH_4Br proceed with retention of configuration (probably, S_E2) [146].

Since in organometallic reactions of the S_E type the role of the electrophile can be played by negatively charged entities (I_3^-, $HgBr_3^-$ etc.) one may conclude that (1) the controlling factor is not the electrophilicity of the electrophilic agent, but its ability to enter into nucleophilic coordination with the metal atom, and (2) electrophilic attack on a carbon atom proceeds only after nucleophilic coordination [77,78].

Nucleophilic catalysis has opened some new synthetic pathways in organometallic chemistry. Thus, change from the stronger electrophile Ph_3CClO_4 to the weaker electrophile Ph_3CBr, which is capable of nucleophilic coordination, enables alkylations to be carried out with a series of organomercury compounds [79-82]. The catalytic reaction of organomercury compounds with acyl halides is a convenient method for synthesis of unsymmetrical ketones [83]. The reactions of RHgX or R_2Hg (R = C_6F_5, CH_3COCH_2, $(CF_3)_2CH$, CCl_3, PhCHCOO) with trinitrobenzene in the presence of I^-, or of $RSnMe_3$ (R = CH_3COCH_2, PhC≡C, cyclo-C_5H_5, C_6F_5, etc.) in DMSO (which act as nucleophilic catalysts) result in quantitative yields of Meisenheimer's complexes $[C_6H_3(NO_2)_3R]^-$ [84].

The phenomenon of nucleophilic catalysis is closely associated with complex formation. The NMR technique was used for studies of structures and complexation properties of organo-mercury and -tin compounds. [see refs. 85, 86 for reviews]. Dimethylmercury [87,88], diethylmercury [89], diphenylmercury [90], dibenzylmercury [91], unsymmetrical phenyl- [92,93], benzyl- [92,94-96], trifluoromethyl- [97] and other mercury derivatives, and also tetramethyl [89] derivatives of silicon, germanium, tin, and lead, a variety of methyltin halides [98], trimethyltrifluoromethyltin and other organotin compounds, are among the substances studied by such techniques. It has been shown [85,86] that the most informative parameters in NMR spectra of the organometallic compounds are the heteronuclear spin coupling constants of metal with ^1H, ^{13}C and ^{19}F isotopes; these constants characterize the electron density distribution in the organometallic molecules and their complexes with electron-donor ligands.

The study of solvent effects on kinetics and mechanims by NMR techniques, has been started recently and the reactions of dibenzylmercury with trifluoromethylmercury salts and of tetramethyltin with trichloromethyltin was chosen as a model [99—100].

$$Bz_2Hg + CF_3HgX(HgX_2) \rightarrow BzHgCF_3(X) + BzHgX$$

$$R_4Sn + RSnX_3 \rightarrow R_2SnX_2 + R_3SnX$$

The preliminary data indicate that the reactions have the S_Ei mechanism in non-polar and poorly solvating solvents. In polar and strongly solvating solvents CF_3HgX and $RSnX_3$ give solvate complexes, which interact with the fully organometallic compounds either in the form of molecular complexes or, more probably, as ion pairs. Formation of solvate complexes in solution has been confirmed by means of both NMR spectroscopy [91,97,98], and isolation of the solid molecular complexes [101-103]. The structures of such complexes have been studied by IR [103], Mössbauer [104] and nuclear quadrupole resonance [105] techniques.

Reactions of R_2Hg, R_4Sn, R_4Ge and R_4Si (R = alkyl) with triarylmethane derivatives

These reactions result in formation of olefins and triarylmethane owing to reduction of the Ar_3C^+ ion by hydride ion from the β-position of the alkyl group [138-140]:

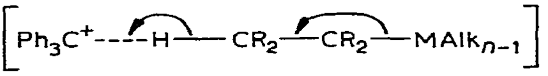
$$Ar_3CX + (R^1R^2CHCHR^3)_nM \rightarrow Ar_3CH + R^1R^2C{=}CHR^3 + (R^1R^2CHCHR^3)_{n-1}MX$$

(M = Hg, Sn, Ge, Si; X = ClO_4, BF_4, $HgBr_3$, $ZnCl_2Br$; Ar = Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$; R^1, R^2, R^3 = H, CH_3)

When there is no β-hydrogen atom, dealkylation takes place, e.g.:

$$(CH_3)_2Hg \xrightarrow{Ph_3C^+\,ClO_4^-} Ph_3CCH_3 \xleftarrow{Ph_3C^+\,ClO_4^-} (CH_3)_4Sn$$

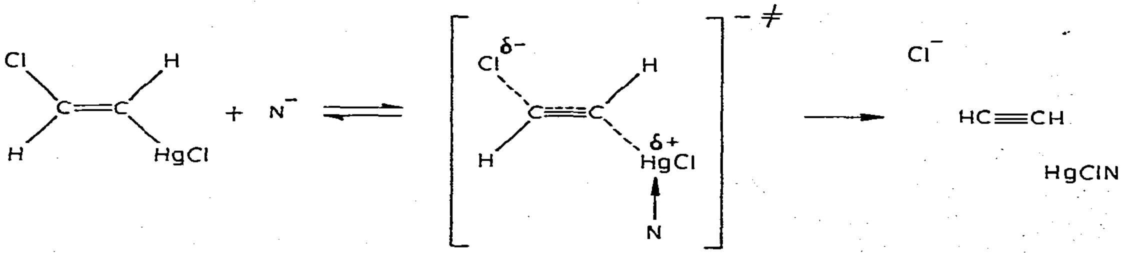
The rate of the hydride transfer



decreases steeply in the order [140,141]: $R_2Hg > R_4Sn > R_4Ge > R_4Si$. For structure and solvent effects in such reactions see ref. 147.

S_E1 reactions at sp^2-carbon atoms

It has been found that both proto- and iodo-demercurations of *trans*-β-chlorovinylmercury chloride have an S_E2 mechanism in dioxane, but the mechanism changes in DMSO to $S_E1(N)$ [106-108]. Since the stability of the carbanion $ClCH{=}CH^-$ is relatively low (pK_a 31.5), both S_E2 and $S_E1(N)$ mechanisms occur, DMSO acting as a nucleophile in the latter case. With nucleophiles stronger than DMSO, e.g. halide anions, elimination of acetylene takes place [142]. It may be assumed that the transition state in this reaction is similar to that of the $S_E1(N)$ reaction. In this case the carbanion center is stabilized by chloride anion elimination from the β-position, and this leads to acetylene formation.



The S_E1 reaction of β-chlorovinylmercury chloride proceeds with retention of geometrical configuration.

In forthcoming work we intend to study the kinetics and stereochemistry of S_E reactions at sp^2 carbon atoms using the model compounds synthesised by us by direct mercuration of vinyl compounds [143-145]:

$$\text{ArAr'C=CH}_2 + \text{Hg(OCOCF}_3)_2 \xrightarrow{\text{CH}_3\text{CN}} \text{ArAr'C=CHHgX}$$

The isotopic exchange of phenylmercury bromide with ^{203}HgBr$_2$ has an S_E2 mechanism in benzene, methanol, DMF, DMSO and other solvents [109].

Pentafluorophenylmercury bromide reacts with ^{203}HgBr$_2$ in DMSO by the $S_E1(N)$ mechanism [110].

$$\text{C}_6\text{F}_5\text{HgBr} + \overset{\star}{\text{Hg}}\text{Br}_2 \overset{\text{DMSO}}{\rightleftharpoons} \text{C}_6\text{F}_5\overset{\star}{\text{Hg}}\text{Br} + \text{HgBr}_2$$

The reaction is of first order overall (first in organometallic compound and zero in mercury bromide).

The role of the ion pair in S_E reactions

Recently we studied a number of reactions of mercuro- [111,112] and halo-destannation [113-117] of organotin compounds RSn(CH$_3$)$_3$ over a wide range of variation in the nature of the R groups (R = CH$_3$, n-C$_4$H$_9$, C$_6$H$_5$, C$_6$H$_5$CH$_2$, CH$_2$=CHCH$_2$, C$_6$F$_5$, C$_6$H$_5$C≡C, C$_9$H$_7$ (indenyl), CH$_3$COCH$_2$, cyclo-C$_5$H$_5$, CN). The reactions were carried out in methanol, DMSO and carbon tetrachloride.

Some of the organotin compounds (R = CH$_3$, n-C$_4$H$_9$, C$_6$H$_5$, C$_6$H$_5$CH$_2$, C$_6$F$_5$, CF$_3$) react in polar solvents by the S_E2 mechanism. This follows from kinetic data and the nature of the reactivity of RSn(CH$_3$)$_3$ compounds as the nature of the breaking bond, C—Sn is changed. On the other hand, the lack of compensation effect and of linearity in free energy changes in the series studied suggests a continuous change in structure of the transition state, depending on the natures of the R group of the electrophile, and of the solvent [113,114].

Quite a different mechanism has been observed for iododestannation of compounds with strong electron-withdrawing groups (R = C$_6$H$_5$C≡C, C$_9$H$_7$, cyclo-C$_5$H$_5$, CH$_3$COCH$_2$, CN); in this reaction the cleavage of the least nucleophilic group R occurs, and the reaction rate increases so greatly that stop-flow techniques have to be used for rate studies [115,116]. With R = C$_6$H$_5$C≡C or C$_9$H$_7$ the reaction is bimolecular and of first order in each of the reagents. However, the rates of reaction of both compounds with iodine (as well as with mercury chloride) are much higher than the rates of iododestannation of C$_6$H$_5$Sn(CH$_3$)$_3$ and CH$_2$=CHSn(CH$_3$)$_3$, the most reactive compounds in the S_E2 reactions. We suggest that these results can be explained by proposing a hypothetical S_E2 mechanism involving participation of contact-ion pair, which is formed in a preequilibrium step and interacts with the electrophile in the rate-determining step.

The kinetics for (CN)Sn(CH$_3$)$_3$, CH$_3$COCH$_2$Sn(C$_2$H$_5$)$_3$ and cyclo-C$_5$H$_5$Sn(CH$_3$)$_3$ are even more unusual: the reaction is of first order in organotin compounds and zero order in iodine, and its rate, with exception of R = cyclo-C$_5$H$_5$, does not depend on the concentration of added iodide ion. The iododestannations of (CN)Sn(CH$_3$)$_3$ and CH$_3$COCH$_2$Sn(C$_2$H$_5$)$_3$ are probably the first examples of the S_E1 mechanism in organotin compounds. It has been assumed that ionization of the organotin compound in the rate-determining step results in an ion pair which reacts with iodine in the fast step.

It should be noted that the assumption of the participation of ion pairs in such reactions allows us not only to explain the "abnormal" high reaction rates of the compounds with strong electron-withdrawing substituents, but also, as for nucleophilic substitutions [118], to unify the electrophilic substitution mechanisms in organometallic compounds [113]:

$$RM \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^- M^+ \underset{I_2}{\overset{k_2}{\rightarrow}} RI + MI$$

The type of mechanism depends on the rate constants ratio: if $k_2[I_2] \gg k_{-1}$, the S_E1 mechanism occurs, and if $k_2[I_2] \ll k_{-1}$, the ion pair S_E2 mechanism [$S_E2(R^- M^+)$] takes place. For compounds with strong electron-releasing groups R the classical S_E2 mechanism may operate.

If the pK_a values of the respective CH-acids, RH, are used as a criterion of the reaction mechanism, then the following pattern can be expected. The compounds with the most electron-releasing R groups will react via the classical S_E2 mechanism; however, as the pK_a(RH) value decreases, the ionization ability of the organometallic compound will increase, which should lead to the S_E2-$(R^- M^+)$ mechanism. As the stability of the carbanion, R^-, is further increased, either the S_E1 mechanism, or the extreme $S_E2(R^- M^+)$ mechanism, the bimolecular reaction with the electrophiles of the ion pairs from the fully ionized compounds, may become more advantageous.

The ion pair approach has been used by us to explain the data on iododestannation in carbon tetrachloride [117]. With the compounds with strong electron-withdrawing groups (R = CN, cyclo-C_5H_5, C_9H_7) the reaction is overall of second order, first in each of the reagents; the reaction rates are very high (K_2 ca. 10^2 to 10^3 mol^{-1} s^{-1}). The other compounds react by a trimolecular mechanism (second order in iodine) agreeing with the results for aryltrialkylstannanes [119]. This can be explained in terms of the base $S_E2(R^- M^+)$ mechanism if we assume that contact ion pairs may be formed even in such a low polar solvent as carbon tetrachloride.

There is no direct experimental evidence at present for the participation of ion pairs in S_E reactions discussed above*, while the existence of contact and solvent-separated ion pairs has been demonstrated for organic compounds of alkali metals, the possibility of participation of ion pairs in S_E reactions of other organometallic compounds was not discussed until recently.

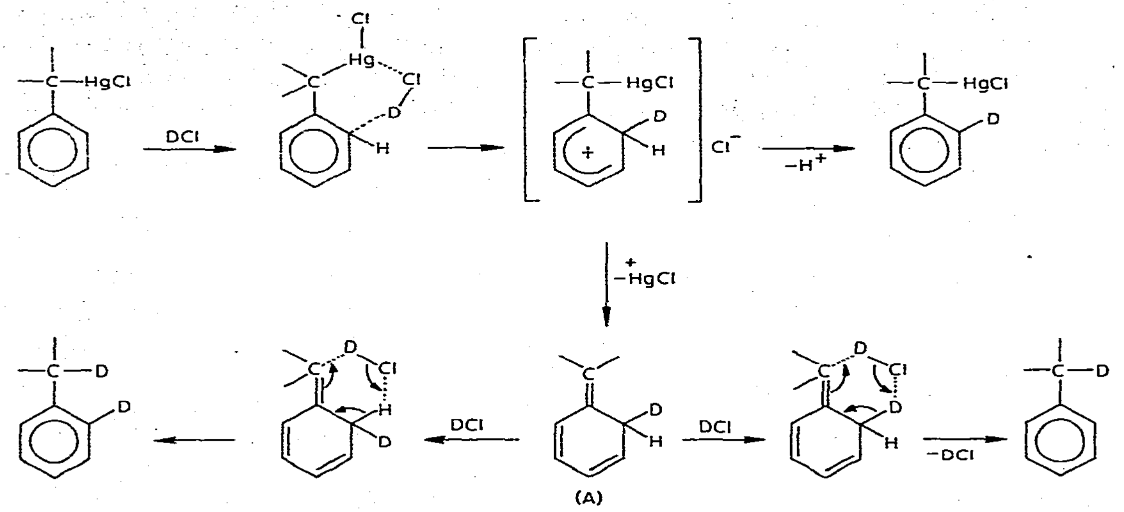
Rigorous evidence for ion pair participation in S_E reactions is an important immediate task. We hope that, stereochemical studies will be used this field in addition to kinetics.

S_E reactions in benzyl organometallic compounds

The reaction of BzHgCl with DCl in dioxane gives the following compounds under conditions of pseudomonomolecularity: *o*-$DC_6H_4CH_2HgCl$ (I), $PhCH_3$ (II), $PhCH_2D$ (III), *o*-$DC_6H_4CH_2D$ (IV). In I and in IV, deuterium is found only in *ortho* positions. The following mechanism has been proposed for this reaction [12]:

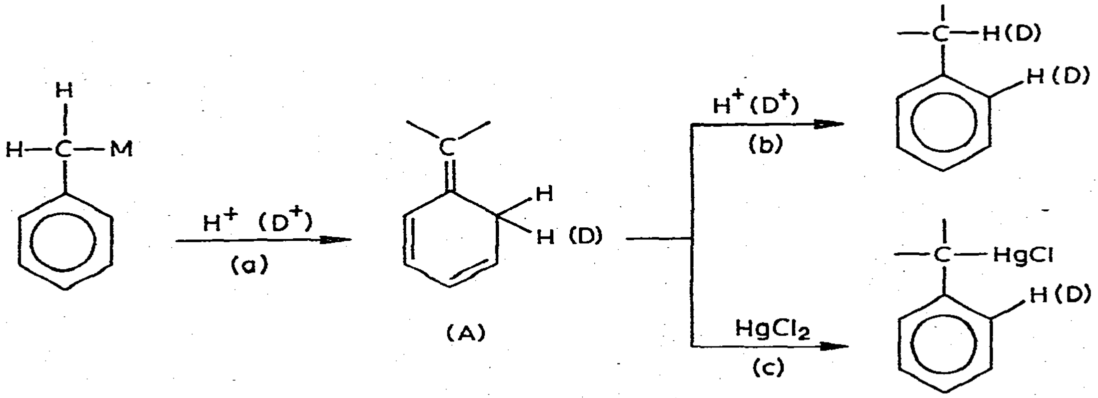
---

* For S_N reactions see, for example, ref. 121.



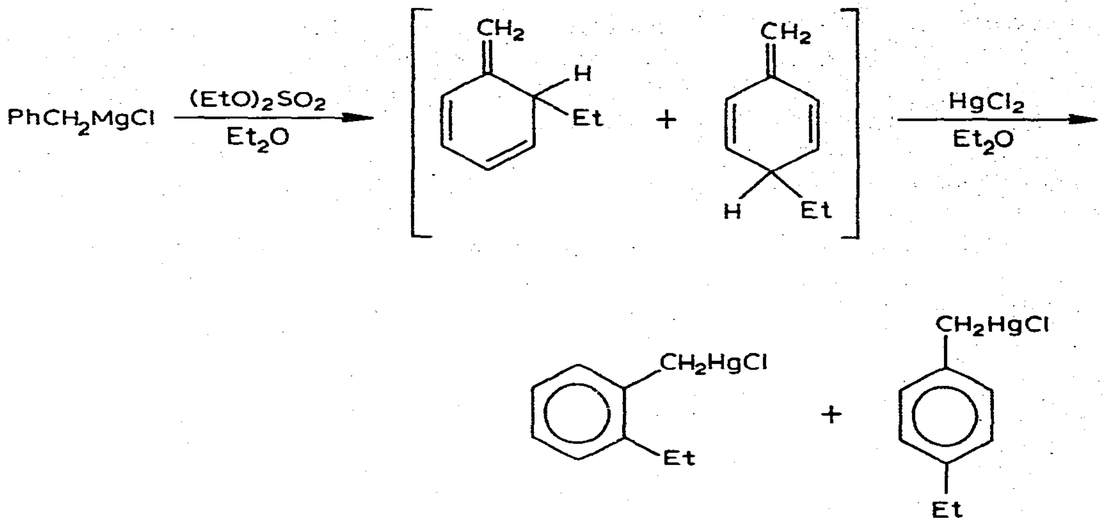
This mechanism is consistent with the more recent data on deutero- [123-127] and acetyl-demercuration [128,129] of ring-substituted benzylmercury chlorides. A similar mechanism has been proposed for deuterodemetallation of tribenzyltin chloride [130].

If the tautomeric form A of toluene is indeed the intermediate in the reactions discussed, one may expect that aromatization of A will occur not only in the reaction with $H^+(D^+)$ but also in reactions with some other electrophilic reagent, deliberately added to the reaction mixtures, e.g. $HgCl_2$ (reaction c):



Addition of $HgCl_2$ to the reaction mixture of $Bz_3SnCl + DCl$ does result indeed in BzHgCl with deuterium in the *ortho*-position. Mercury bromide also acts as an electrophilic trap of the arene tautomer.

Ethyl-substituted methylenecyclohexadienes also undergo the "aromatizing metallation" readily [131].

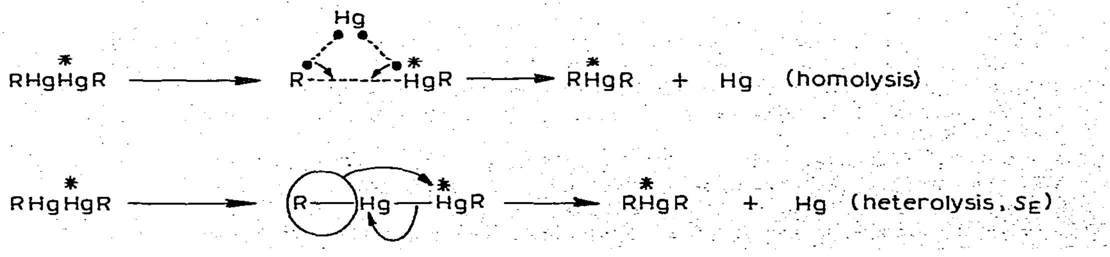


"Aromatizing metallation" may be expected to provide new routes for synthesis of benzyl-organometallic compounds.

Exchange reactions of the type $R_nM + M'$

Mercury isotope exchanges $RHgR' + \overset{*}{Hg} \rightleftharpoons R\overset{*}{Hg}R' + Hg$ were discovered at the same time as the analogous "one-alkyl" isotopic exchange $RHgX + \overset{*}{Hg} \rightleftharpoons R\overset{*}{Hg}X + Hg$; both types of reaction showed very similar qualitative behaviour [132,133]. The reactions proceed under very mild conditions, which excludes the possibility of a free radical mechanism. The isotopic exchange at a saturated C-atom gives a product with retention of configuration [22]. During the exchange with $\overset{*}{Hg}$, $p\text{-}O_2NC_6H_4HgC_6H_5$ remains chemically unchanged, and no $(C_6H_5)_2\overset{*}{Hg}$ or $(p\text{-}O_2NC_6H_4)_2\overset{*}{Hg}$ was formed in the reaction [133].

It has been shown by use of pulsed electrochemical techniques that R_2Hg's are in equilibrium with "organic calomels" on mercury surface [134]: $R_2Hg + Hg \rightleftharpoons RHgHgR$. "Organic calomels" are very unstable species with life-times of ca. 10^{-2} to 10^{-5} sec, depending on the nature of R [135]. These species are apparently intermediates in the mercury isotope exchanges discussed. It is an open question whether the calomels are converted homolytically or heterolytically into the products of the isotopic exchange but in any case neither free radicals nor free ions are involved in these reactions:



The effect of substituents in the aromatic ring is typical for S_E reactions.

It has been shown by use of the galvanostatic method that the transmetallation reaction, $R_2Tl^+ + Hg \rightarrow R_2Hg + Tl^+$, proceeds through the intermetallic cations, RTl^+HgR, which are isoelectronic with organic calomels [136].

Intermediates of the R_nMHgR types may be assumed to be quite common in transmetallation reactions involving mercury metal or organomercury compounds.

Proceeding from this assumption we discovered a new route for synthesis of σ-Pt and σ-Pd organometallic compounds, the use of which is probably limited only by the availability of the respective organomercury compounds [137]:

$$L_nPt^0 + RHgR' \longrightarrow L_2Pt(HgR)R' + (n-2)L \longrightarrow$$

$$L_2PtRR' + Hg^0 + (n-2)L$$

$(L = Ph_3P)$

The key step of the process is, doubtless, electron transfer from zero-valent platinum or palladium complexes to organomercury compounds, RHgX or R_2Hg. Evidence was obtained that compouds with Hg—Pt or Hg—Pd bonds are intermediates in these reactions and $L_2Pt(HgCF_3)CF_3 \cdot CH_3COCH_3$ is stable.

It was found, that this method may be extended to low-valent derivatives of other transition metals, e.g. rhodium(I), iridium(I), as well as to those of other non-transition metals, e.g. tin and lead.

References

1 O.A. Reutov, On the Mechanism of Electrophilic Substitution at Saturated Carbon, Uspekhi Khim., 36 (1967) 414.
2 O.A. Reutov, Elektrophile Substitution bei quecksilberorganischen Verbindungen. Fortschr. Chem. Forsch, 8 (1967) 61.
3 O.A. Reutov and I.P. Beletskaya, Reaction Mechanisms of Organometallic Compounds, North-Holland Publ. Company, Amsterdam, 1968, Chapter II.
4 O.A. Reutov, I.P. Beletskaya and V.I. Sokolov, Reaction Mechanisms of Organometallic Compounds, Publishing House "Khimia", Moscow, 1972, Chapter I.
5 O.A. Reutov and I.P. Beletskaya, Dokl. Akad. Nauk SSSR, 131 (1960) 853.
6 O.A. Reutov, I.P. Beletskaya and R.E. Mardaleishvili, Zh. Fiz. Khim., 33 (1959) 152.
7 O.A. Reutov, I.P. Beletskaya and R.E. Mardaleishvili, Zh. Fiz. Khim., 33 (1959) 1952.
8 O.A. Reutov, I.P. Beletskaya and R.E. Mardaleishvili, Dokl. Akad. Nauk SSSR, 116 (1957) 617.
9 A.N. Nesmeyanov, O.A. Reutov and S.S. Poddubnaya, Dokl. Akad. Nauk SSSR, 88 (1953) 479.
10 O.A. Reutov, I.P. Beletskaya and G.A. Artamkina, Zh. Org. Khim., 34 (1964) 2817.
11 O.A. Reutov, Dokl. Akad. Nauk SSSR, 163 (1965) 909.
12 O.A. Reutov, I.P. Beletskaya and G.A. Artamkina, Zh. Fiz. Khim., 36 (1962) 2582.
13 I.P. Beletskaya, G.A. Artamkina and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 1737.
14 I.P. Beletskaya, G.A. Artamkina and O.A. Reutov, Dokl. Akad. Nauk SSSR, 149 (1963) 90.
15 S. Winstein, T.G. Traylor and C. Garner, J. Amer. Chem. Soc., 77 (1955) 3741.
16 A.N. Nesmeyanov, O.A. Reutov, U-Yang-Tsei and Lu-Tsing-Chgu, Izv. Akad. Nauk SSSR, Ser. Khim., (1959) 880.
17 H.B. Charman, E.D. Hughes and C.K. Ingold, J. Chem. Soc., (1959) 2523, 2530.
18 H.B. Charman, E.D. Hughes and C.K. Ingold, Chem. Ind., (1958) 1517.
19 F.R. Jensen, J. Amer. Chem. Soc., 82 (1960) 2469.
20 O.A. Reutov and E.V. Uglova, Izv. Akad. Nauk SSSR, Ser. Khim., (1959) 757, 1691.

21 N.A. Nesmeyanov and O.A. Reutov, Tetrahedron, 20 (1964) 2803.
22 O.A. Reutov, P. Knoll and U-Yang-Tsey, Dokl. Akad. Nauk SSSR, 120 (1958) 1052.
23 O.A. Reutov, T.A. Smolina, U-Yang-Tsey and Yu.N. Bubnov, Nauchn. Vyssh. Shk., 1 (1958) 354.
24 O.A. Reutov, Angew. Chem., 72 (1960) 198.
25 O.A. Reutov, Y.I. Sokolov and I.P. Beletskaya, Dokl. Akad. Nauk SSSR, 136 (1960) 691.
26 O.A. Reutov, V.I. Sokolov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1961) 123, 1217.
27 O.A. Reutov, V.I. Sokolov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1961) 1427.
28 O.A. Reutov, V.I. Sokolov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1961) 1561.
29 O.A. Reutov, V.I. Sokolov, I.P. Beletskaya and Yu.S. Riabokobilko, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 965.
30 O.A. Reutov, B. Praisnar, I.P. Beletskaya and V.I. Sokolov, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 970.
31 O.A. Reutov, V.I. Sokolov and I.P. Beletskaya, Correlation equations in organic chemistry, Vol. 1, Tartu, 1962, p. 342.
33 E.D. Hughes, C.K. Ingold, F.G. Thorpe and H.C. Volger, J. Chem. Soc., (1961) 1133.
34 H.B. Charman, E.D. Hughes, C.K. Ingold and H.C. Volger, J. Chem. Soc., (1961) 1142.
35 C.K. Ingold, Helv. Chim. Acta, 47 (1964) 1191.
36 E.D. Hughes and H.C. Volger, J. Chem. Soc., (1961) 2359.
37 E.D. Hugher, C.K. Ingold and R.M.G. Roberts, J. Chem. Soc., (1964) 3900.
38 O.A. Reutov, T.A. Smolina and V.A. Kalyavin, Dokl. Akad. Nauk SSSR, 139 (1961) 389.
39 O.A. Reutov, T.A. Smolina and V.A. Kalyavin, Zh. Fiz. Khim., 36 (1962) 119.
40 V.A. Kalyavin, T.A. Smolina and O.A. Reutov, Dokl. Akad. Nauk SSSR, 155 (1964) 596.
41 V.A. Kalyavin, T.A. Smolina and O.A. Reutov, Dokl. Akad. Nauk SSSR, 156 (1964) 95.
42 V.A. Kalyavin, T.A. Smolina and O.A. Reutov, Dokl. Akad. Nauk, SSSR, 157 (1964) 919.
43 T.A. Smolina, V.A. Kalyavin and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 2235.
44 O.A. Reutov, Hu Hung Weng, T.A. Smolina and I.P. Beletskaya, Zh. Fiz., Khim., (1961) 2424.
45 O.A. Reutov, T.P. Karpov, E.V. Uglova and V.A. Malyanov, Dokl. Akad. Nauk SSSR, 134 (1960) 360.
46 T.P. Karpov, V.A. Malyanov, E.V. Uglova and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1964) 1518.
47 H.B. Charman, E.D. Hughes, C.K. Ingold and F.G. Thorpe, J. Chem. Soc., (1961) 1121.
48 F.R. Jensen and D.D. Davis, J. Amer. Chem. Soc., 93 (1971) 4048.
49 I.P. Beletskaya, K.P. Butin and O.A. Reutov, Organometal. Chem. Rev, A, 7 (1971) 51-79.
50 I.P. Beletskaya, G.A. Artamkina and O.A. Reutov, Dokl. Akad. Nauk SSSR, 153 (1963) 588.
51 I.P. Beletskaya, O.A. Maximenko and O.A. Reutov, Zh. Org. Khim., 2 (1966) 1129.
52 I.P. Beletskaya, O.A. Maximenko, V.B. Vol'eva and O.A. Reutov, Zh. Org. Khim., 2 (1966) 1132.
53 V.A. Kalyavin, T.A. Smolina and O.A. Reutov, Dokl. Akad. Nauk SSSR, 156 (1964) 95.
54 I.P. Beletskaya, T.P. Fetisova and O.A. Reutov, Dokl. Akad. Nauk SSSR, 155 (1964) 1095.
55 J.R. Coad and M.D. Johnson, J. Chem. Soc. B (1967) 633.
56 D. Dodd and M.D. Johnson, J. Chem. Soc. B (1969) 1071.
57 C.J. Cooksey, D. Dodd and M.D. Johnson, J. Chem. Soc. B (1971) 1380.
58 M.D. Johnson and N. Winternon, J. Chem. Soc., A, (1970) 511.
59 N.A. Nesmeyanov, S.T. Berman, L.D. Ashkinadze, L.A. Kazitsina and O.A. Reutov, Zh. Org. Khim., 4 (1968) 1685.
60 N.A. Nesmeyanov, V.M. Novikov and O.A. Reutov, J. Organometal. Chem., 4 (1965) 202.
61 N.A. Nesmeyanov, A.V. Kalinin and O.A. Reutov, Zh. Org. Khim., 5 (1969) 1508.
62 N.A. Nesmeyanov, A.V. Kalinin and O.A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 98.
63 K.P. Butin, I.P. Beletskaya and O.A. Reutov, Electrokhimia, 2 (1966) 635.
64 K.P. Butin, I.P. Beletskaya, A.N. Kashin and O.A. Reutov, Dokl. Akad. Nauk SSSR, 175 (1967) 1055.
65 K.P. Butin, I.P. Beletskaya, A.N. Kashin and O.A. Reutov, J. Organometal. Chem., 10 (1967) 197.
66 O.A. Reutov, K.P. Butin and I.P. Beletskaya, Bull. Inst. Politeh. Iasi, 26 (20), II, issue 3-4 (1970) 33.
67 O.A. Reutov, K.P. Butin and I.P. Beletskaya, Usp. Khim., 43 (1974) 33.
68 K.P. Butin, A.N. Kashin, I.P. Beletskaya, L.S. German and Vl. R. Polishchuk, J. Organometal. Chem., 25 (1970) 11.
69 V.I. Stanko, V.I. Bregadze, A.I. Klimova, O.Yu. Okhlobistin, A.A. Kashin, K.P. Butin and I.P. Beletskaya , Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 421.
70 A.N. Kashin, K.P. Butin, V.I. Stanko and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1917.
71 K.P. Butin, L.G. Yudin, A.I. Pavluchenko, I.P. Beletskaya and A.N. Kost, Zh. Org. Khim., 7 (1971) 2586.
72 K.P. Butin, A.N. Kashin, I.P. Beletskaya and O.A. Reutov, J. Organometal. Chem., 16 (1969) 27.
73 I.P. Beletskaya, K.P. Butin and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 1618.

74 K.P. Butin, V.N. Shishkin, I.P. Beletskaya and O.A. Reutov, Dokl. Akad. Nauk SSSR, 218 (1974) 371.
75 K.P. Butin, I.P. Beletskaya and O.A. Reutov, J. Organometal. Chem., 64 (1974) 323.
76 I.P. Beletskaya, T.A. Azizian and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 1332.
77 O.A. Reutov and I.P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 955.
78 I.P. Beletskaya, A.L. Kurz and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 2207.
79 I.P. Beletskaya, O.A. Maximenko and O.A. Reutov. Dokl. Akad. Nauk SSSR., 168 (1966) 333.
80 I.P. Beletskaya, O.A. Maximenko and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 662.
81 I.P. Beletskaya, O.A. Maximenko and O.A. Reutov, Zh. Org. Khim., 2 (1966) 1137.
82 I.P. Beletskaya, V.B. Vol'eva and O.A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 360; 204 (1972) 93.
83 I.P. Beletskaya, A.L. Kurz, I.A. Savchenko and O.A. Reutov, J. Organometal. Chem., 17 (1969) P21.
84 I.P. Beletskaya, G.A. Artamkina and O.A. Reutov, J. Organometal. Chem., 42 (1972) C16.
85 V.S. Petrosyan and O.A. Reutov, Pure Appl. Chem., 37 (1974) 147.
86 V.S. Petrosyan and O.A. Reutov, J. Organometal. Chem., 76 (1974) 123.
87 V.S. Petrosyan, B.P. Bespalov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1967) 2127.
88 V.S. Petrosyan, A.S. Voyakin and O.A. Reutov, Zh. Org. Khim., 6 (1970) 889.
89 V.S. Petrosyan, N.S. Yashina and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1018.
90 V.S. Petrosyan and O.A. Reutov, Zh. Org. Khim., 3 (1967) 2074.
91 V.S. Petrosyan, V.I. Bakhmutov and O.A. Reutov, J. Organometal. Chem., 72 (1974) 79.
92 V.S. Petrosyan and O.A. Reutov, Dokl. Akad. Nauk SSSR, 180 (1968) 876.
93 V.S. Petrosyan and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 1962.
94 V.S. Petrosyan, V.I. Rozenberg, Yu.G. Bundel and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 1958.
95 V.S. Petrosyan and O.A. Reutov, Izv. Akad. Nauk. SSSR, Ser. Khim., (1970) 1403.
96 V.S. Petrosyan, V.I. Bakhmutov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1428.
97 V.S. Petrosyan, V.I. Bakhmutov and O.A. Reutov, J. Organometal. Chem., 72 (1974) 87.
98 V.S. Petrosyan, N.S. Yashina, V.I. Bakmutov and O.A. Reutov, J. Organometal. Chem., 72 (1974) 71.
99 V.S. Petrosyan, A.B. Permin and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1305.
99a V.S. Petrosyan and O.A. Reutov, J. Organometal. Chem., 52 (1973) 307.
99b V.S. Petrosyan, S.M. Sakembayeva, V.I. Bakhmutov and O.A. Reutov, Dokl. Akad. Nauk SSSR, 209 (1973) 1117.
99c V.S. Petrosyan, S.M. Sakembayeva and O.A. Reutov, Izv. Akad. Nauk SSSR., Ser. Khim., (1973) 1403.
100 V.S. Petrosyan, S.G. Sakharov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 743.
101 V.S. Petrosyan, V.V. Bashilov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 481.
102 V.S. Petrosyan, N.S. Yashina and O.A. Reutov, J. Organometal. Chem., 52 (1973) 315.
103 V.S. Petrosyan, V.I. Bachmutov and O.A. Reutov, J. Organometal. Chem., in press.
104 V.S. Petrosyan, N.S. Yashina, S.G. Sakharov and O.A. Reutov, J. Organometal. Chem., 52 (1973) 333.
105 V.S. Petrosyan, N.S. Yashina, O.A. Reutov, E.V. Brykhova, and G.K. Semin, J. Organometal. Chem., 52 (1973) 321.
106 I.P. Beletskaya, V.I. Karpov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 1135.
107 I.P. Beletskaya, V.I. Karpov, V.A. Moskalenko and O.A. Reutov, Dokl. Akad. Nauk SSSR, 162 (1965) 86.
108 O.A. Reutov, I.P. Beletskaya, V.S. Petrosyan and Z.V. Savinyukh, Tetrahedron Lett., 4 (1969) 485.
109 O.A. Reutov, I.P. Beletskaya and I.I. Zakharicheva, Zh. Org. Khim., 5 (1969) 793; 5 (1969) 798; 5 (1969) 2081; 5 (1969) 2087.
110 I.P. Beletskaya, I.I. Zakharicheva and O.A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 837.
111 I.P. Beletskaya, A.N. Kashin, A.Ts. Malkhasyan and O.A. Reutov, Zh. Org. Khim., 9 (1973) 1089.
112 A.N. Kashin, I.P. Beletskaya, A.Ts. Malkhasyan and O.A. Reutov, Zh. Org. Khim., 9 (1973) 1098.
113 I.P. Beletskaya, A.N. Kashin, A.Ts. Malkhasyan and O.A. Reutov, Zh. Org. Khim., 9 (1973) 2215.
114 A.N. Kashin, I.P. Beletskaya, A.Ts. Malkhasyan and O.A. Reutov, Zh. Org. Khim., 10 (1974) 673.
115 I.P. Beletskaya, A.N. Kashin, A.Ts. Malkhasyan, A.A. Solovyanov and O.A. Reutov, Zh. Org. Khim., 10 (1974) 678.
116 I.P. Beletskaya, A.N. Kashin, A.Ts. Malkhasyan, A.A. Solovyanov and O.A. Reutov, Zh. Org. Khim., 10 (1974) 1566.
117 A.N. Kashin, I.P. Beletskaya, A.Ts. Malkhasyan, A.A. Solovyanov and O.A. Reutov, Zh. Organich. Khim., 10 (1974) 2241.
118 R.A. Sneen and J.W. Larsen, J. Amer. Chem. Soc., 91 (1969) 362.
119 R.W. Bott, C. Eaborn and J.A. Waters, J. Chem. Soc., (1963) 681.
120 J. Smid, Angew. Chem., Intern. Ed., 11 (1972) 112.

121 S. Winstein, B. Appel, R. Baker and A. Diaz, Chem. Soc. Spec. Publ., 9 (1965) 109.
122 Yu.G. Bundel, N.D. Antonova and O.A. Reutov, Dokl. Akad. Nauk SSSR, 166 (1966) 1103.
123 Yu.G. Bundel, V.I. Rosenberg and O.A. Reutov, Izv. Akad. Nauk, Ser. Khim., (1969) 2316.
124 Yu.G. Bundel, V.I. Rosenberg, I.N. Krokhina and O.A. Reutov, Zh. Org. Khim., 6 (1970) 1519.
125 Yu.G. Bundel, T.V. Gavrilova, V.I. Rosenberg and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1382.
126 Yu.G. Bundel, V.I. Rosenberg and O.A. Reutov, Izv. Akad. Nauk SSSR, (1970) 918.
127 Yu.G. Bundel, V.I. Rosenberg, G.V. Gavrilova, E.A. Arbuzova and O.A. Reutov, Izv. Akad. Nauk SSSR, (1970) 1155.
128 Yu.G. Bundel, V.I. Rosenberg, A.L. Kurz, N.D. Antonova and O.A. Reutov, Dokl. Akad. Nauk SSSR, 187 (1969) 1290.
129 Yu.G. Bundel, V.I. Rosenberg, A.L. Kurz, N.D. Antonova and O.A. Reutov, J. Organometal. Chem., 18 (1969) 209.
130 Yu.G. Bundel, V.A. Nikanorov, M. Abazid and O.A. Reutov, Izv. Akad. Nauk SSSR, (1973) 233.
131 V.A. Nikanorov, V.I. Rosenberg, R.I. Gorbacheva and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim, (1974) 113.
132 O.A. Reutov and U-Yang-Tsei, Dokl. Akad. Nauk SSSR, Ser. Khim., 117 (1957) 1003.
133 O.A. Reutov and G.M. Ostapchuk, Dokl. Akad. Nauk SSSR, Ser. Khim., 117 (1957) 826.
134 K.P. Butin, A.B. Ershler, V.V. Strelets, A.N. Kashin, I.P. Beletskaya and O.A. Reutov, J. Organometal. Chem., 64 (1974) 171.
135 A.N. Kashin, A.B. Ershler, V.V. Strelets, K.P. Butin, I.P. Beletskaya and O.A. Reutov, J. Organometal. Chem., 39 (1972) 237.
136 K.P. Butin, V.V. Strelets, I.P. Beletskaya and O.A. Reutov, J. Organometal. Chem., 64 (1974) 189.
137 V.I. Sokolov, V.V. Bashilov, L.M. Anishchenko and O.A. Reutov, J. Organometal. Chem., 71 (1974) C41.
138 E.V. Uglova, O.A. Reutov and V.D. Makhayev, Dokl. Akad. Nauk SSSR, 188 (1969) 833.
139 O.A. Reutov, E.V. Uglova, V.D. Makhayev and V.S. Petrosyan, Zh. Org. Khim., 6 (1970) 2153.
140 O.A. Reutov, E.V. Uglova and V.D. Makhayev, Zh. Org. khim., 8 (1972) 894.
141 J.M. Jerconica and T.G. Traylor, J. Amer. Chem. Soc., 93 (1971) 6278.
142 A.N. Nesmeyanov, A.E. Borisov and I.S. Savel'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1968) 286.
143 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, Dokl. Akad. Nauk SSSR, 188 (1969) 127.
144 V.I. Sokolov, V.V. Bashilov, P.V. Petrovskii and O.A. Reutov, Dokl. Akad. Nauk SSSR, 213 (1973) 1103.
145 V.I. Sokolov, V.V. Bashilov, P.V. Petrovskii, D.A. Lemenovskii, K.I. Granberg and O.A. Reutov, Dokl. Akad. Nauk SSSR, 214 (1974) 393.
146 O.A. Reutov, E.V. Uglova and T.V. Svetlanova, Reports of All Union Çonference on dynamic stereochemistry and conformation analysis, Odessa, 1970, p. 98.