

## TETRAHEDRON REPORT NUMBER 55

### SOME ASPECTS OF ORGANOMETALLIC CHEMISTRY OF NONTRANSITION METALS

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#### 1. INTRODUCTION

The investigation of organometallic compounds is very important for solving of many theoretical organic chemistry problems. For example, the concept of valence has been developed in the studies of alkyl derivatives of various metals (Frankland). The existence of free radicals in the gas phase has been proved unambiguously for the first time by pyrolysis of organolead compounds (Paneth). The elucidation of tautomerism and multiple reactivity has been realized mainly by using the organometallic models (Nesmeyanov).

In the present Report we will discuss the results of an investigation by means of organometallics of the substitution reaction mechanisms at carbon atoms in the various valence states.

The conclusions are of major interest for the development of general theoretical concepts concerning electrophilic and homolytic (in part) substitution at saturated, olefinic or aromatic carbons.

From the viewpoint of the problems under discussion the organic derivatives of nontransition metals have been

conditions but have sufficiently high reactivity. Secondly, the synthetic methods for organomercurials are well developed and a wide range of these compounds are available. Finally, the optically active organic derivatives of mercury (Hg atom is attached to an asymmetric C atom) makes possible the simultaneous study of kinetics and stereochemistry of the model reactions.

#### 2. BIMOLECULAR ELECTROPHILIC SUBSTITUTION REACTIONS AT SATURATED CARBON

The main regularities of electrophilic substitution at a saturated C atom were formulated through the employment of organometallic and predominantly organomercury compounds. Nowadays, various organometallic compounds, including organic derivatives of transition metals come within the scope of these studies.

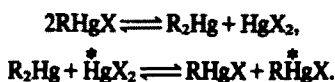
##### 2.1 One-alkyl exchanges

Exchanges between alkylmercury derivatives and inorganic mercuric salts in the isotope exchange of alkyl-

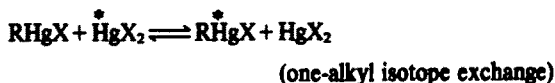
The majority of the results have been obtained for various organic derivatives of mercury because of the advantages of organomercurials as model compounds for these studies. First of all, they are stable under normal

ethanol and phenylmercury bromide with mercuric bromide in pyridine were reported by Nefedov *et al.* The authors proposed a two-step mechanism, involving the formation of a symmetrical organomercury compound

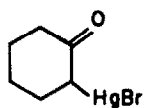
and its subsequent exchange with the inorganic salt:<sup>1</sup>



Further investigation by Reutov *et al.* and by Ingold *et al.* showed that the reaction occurs as a result of direct exchange between the reagents, without preliminary symmetrization:



The effects of structure were investigated in the electrophilic substitution at a saturated carbon in the isotope exchange between organomercury compounds and mercuric halides.<sup>2-5</sup>



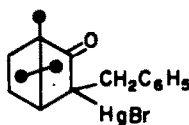
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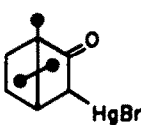
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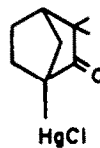
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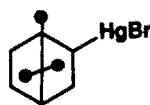
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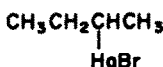
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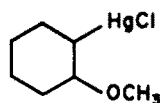
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VII



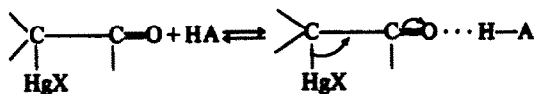
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IX

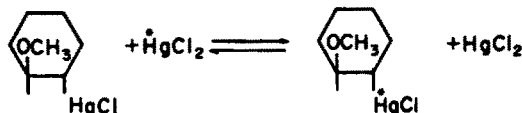
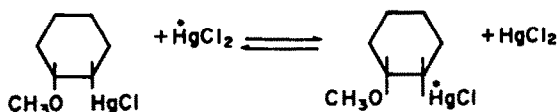
It was found that the  $\alpha$ -mercurated oxo-compounds undergo isotope exchange with <sup>203</sup>Hg-labelled mercuric halide under mild conditions (25°, organic solvents). 1-Chloromercuricamphenylone (VI) is an exception. The remaining organomercuries require more energetic conditions (60–120°). The reactivity decreases in the order: I > IV > II > III > V > VI, VII, VIII, IX.

The reactions of the  $\alpha$ -mercurated oxo-compounds are catalyzed by acids and bases. The action of the acids is evidently due to an interaction between the protons and the CO oxygens, resulting in a weakening of the C-Hg bonds:

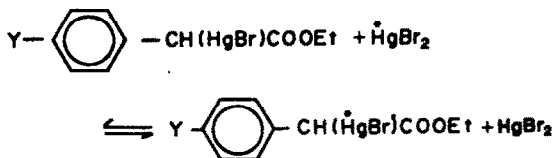


The bases accelerate the reactions by solvating the Hg atoms of the organomercury compounds, which also weakens the C-Hg linkages.

The stereochemistry of the electrophilic substitution, has been studied at a saturated C atom in the isotope exchange of *cis*- and *trans*-2-methoxycyclohexylmercury chloride.<sup>3</sup> The reactions were conducted in dioxan, acetone, and isobutanol. Retention of the starting configuration was observed in every case:



2.1.1 Isotope exchange of the ethyl esters of  $\alpha$ -bromomercuriarylacetic acids with mercuric bromide. Detailed kinetic studies of one-alkyl isotope exchanges were carried out on the reactions of ethyl  $\alpha$ -bromomercuriarylacetic acid and some derivatives with mercuric bromide.<sup>6-10</sup>



These systems allow a study of the kinetic influence of structural factors and a comparison of this influence with that observed in other reactions, e.g. in symmetrization (see Section 3.1.1). However, attention was focussed mainly on the effects exerted on the mechanism and on the reaction rate by the solvent. The solvents with the smallest effect on the organomercury compounds were

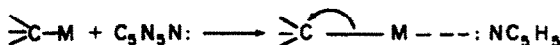
of the greatest interest. A solvent of this kind should have a low polarity and should have no free electron pairs and no electron deficit. Unfortunately, the above reactions could not be studied in inert hydrocarbons which do not have  $\pi$ -electrons (hexane, cyclohexane), because the reactants are practically insoluble in such solvents. For this reason the authors limited themselves to benzene, which is a weak electron donor owing to its aromatic  $\pi$ -system. On the other hand, it was also interesting to perform the reaction in strongly polar, strongly ionizing media, and in strong complex-formers having a basic character. The limitation in the choice of the solvents, specific to this model, is due to the high sensitivity of  $\alpha$ -mercurated esters to even weak acids.

The following solvents were finally tried: pyridine, dimethylformamide, aqueous dioxan, nitromethane, benzene, aqueous ethanol, and dimethyl sulphoxide.

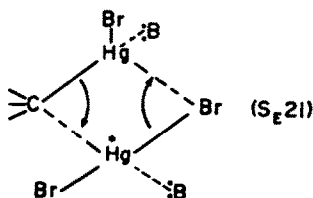
In pyridine, DMF, aqueous ethanol, and benzene the reaction was bimolecular. The values of  $k_2$  obtained at 60° and the activation parameters found from the temperature coefficient of the reaction rate between 50° and 80° are listed in Table 1.

The kinetic effects of some substituents Y were studied in pyridine. It was found that halogen substituents accelerate, and alkyl substituents retard, the above reaction: Br > F > H > CH<sub>3</sub> > t-C<sub>4</sub>H<sub>9</sub>.

It is not very probable that in this case HgBr<sub>2</sub> or HgBr<sup>+</sup> is a directly acting agent. It is known that pyridine complexes are formed very readily with various metal halides, particularly mercuric salts, by means of a dative bond directed from the nitrogen to the metal atom. There can hardly be any doubt that in the presence of an excess of pyridine at elevated temperatures the mercuric bromide exists in the form of a pyridine complex, which is an electrophilic agent. It is also natural to assume that the organomercury compound too is solvated by pyridine molecules. Such solvation should facilitate fission of the C-Hg bond and increase the nucleophilic character of the attacked carbon atom.



The positive effect of the solvation of mercuric bromide is less easy to interpret. It is known that additions of pyridine to other solvents, for example dioxan, will accelerate the exchange. This can only be explained by coordination of a bromine from a molecule of HgBr<sub>2</sub> to the Hg atom in the organomercury compound, i.e. by formation of a closed transition state:



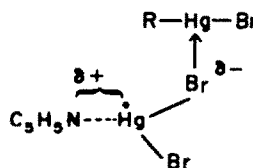
where B is a solvating base, in this example pyridine.

In this case it may be postulated that although the electrophilic power of mercuric bromide in the pyridine complex is reduced, the activity of mercuric bromide as a reagent increases owing to polarization of the Hg-Br bond, which facilitates nucleophilic coordination of a

Table 1. Values of  $k_2$  and the activation parameters for the isotope exchange between PhCH(HgBr)COOEt and HgBr<sub>2</sub>

Solvent	$k_2 \times 10^2$ (l/mole min)	E (Kcal/mole)	$\Delta S^\ddagger$ (e.u.)
Pyridine	6.60	16.30	-25.5
DMF	1.41	16.1	-29.2
80% aq ethanol	6.18	25.1	+7.6
Benzene	0.79 (70°)		

bromine to the Hg atoms in the substrate (see also 7):



It should be noted that the representation of the transition state is necessarily schematic, and does not pretend to reflect the actual stoichiometry with respect to the component B. If a certain number of molecules of B are bound more strongly than others, we should observe a precise kinetic order with respect to B.

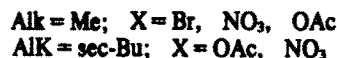
Otherwise we may expect that at sufficiently small concentrations of B the reaction rate will increase with increasing concentration of this reagent. This problem was the subject of discussion between Ingold and Hughes<sup>11,12</sup> on one side, and Swain,<sup>13</sup> supported by Winstein,<sup>14</sup> on the other. So far, the question remains open.

Direct confirmation of the formation of a complex between HgBr<sub>2</sub> and an electron-donating solvent, and confirmation of the fact that this complex is more reactive than the original mercuric bromide, was obtained by studying the isotope exchange in DMF.<sup>13</sup>

2.1.2 Exchanges between alkylmercury derivatives and inorganic mercuric salts. The isotope exchanges reactions in ethanol:



where



was studied by Ingold *et al.*<sup>16-19</sup>

Kinetic studies showed that the isotope exchange occurs in all cases in a single step by direct interaction between the reagents. With overall second order, the order with respect to each component was equal to 1.

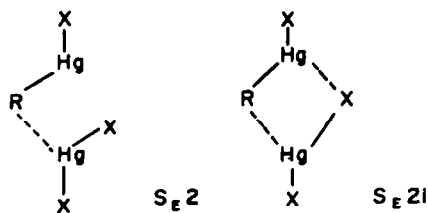
From stereochemical studies of the process, carried out on the optically active *s*-butylmercury acetate subsequently converted into bromide, it was found the

Table 2. Rate constants and relative rates of isotope exchange in MeHgX-HgX<sub>2</sub> system

X	Br	I	OAc	NO <sub>3</sub>
Rel. rate	1	7.9	1000	240000
$k_2 \times 10^4$ (l/mole sec)	0.05 (60°C)	10.1 (100°)	50 (60°)	16.9 (0°)
	1.28 (100°C)			

optical activity of the organomercury remains constant, i.e. that the configuration is fully retained.

On the basis of studies of the isotope exchange in various systems  $\text{MeHgX}-\text{HgX}_2$  attempts were made to solve the problem whether the transition state is open ( $S_E2$  mechanism) or cyclic ( $S_E2i$ ):



It was found that the reaction rate rises sharply with increasing ionic character of the  $\text{Hg}-\text{X}$  bond, i.e. on passing from halides to acetates and nitrates (Table 2).

The following parameters of the Arrhenius equation were determined from these data for the reaction of methylmercury bromide:  $E = -19.8$  kcal/mole and  $\log A = 7.7$ . On the basis of the results the authors tend to favour the non-cyclic form of the transition state ( $S_E2$  mechanism) and reject the possibility of additional coordination of the anion to mercury. However, it is unclear why such coordination does not take place in cases when it would be possible, e.g. with the halides.

When the  $\text{Me}$  radical is replaced by  $n\text{-Bu}$  the reaction rate decreases by a factor of more than 10. The most interesting results were obtained in the study of the influence of salt effects on the rate of the reaction. It was found that lithium nitrate exerted a "normal" salt effect, and in two systems  $\text{MeHgBr}-\text{HgBr}_2$  and  $n\text{-BuHgOAc}-\text{Hg(OAc)}_2$  the logarithm of the rate constant varied linearly with the concentration of the lithium nitrate added. The positive salt effect shows that in both reactions the transition state is more polar than the starting one; the difference in polarity is smaller in the case of the acetates, and the observed effect of the added salt is correspondingly smaller in this system.

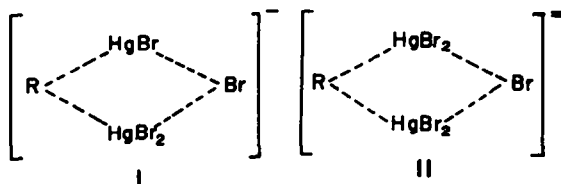
The authors believe that all these facts are easier to reconcile with an open than with a closed transition state, but it should be noted that if the structure of the transition state were in fact open, one should expect a much stronger effect by addition of water than is actually observed. Thus the addition of 10 vol % of water to the ethanol accelerated the isotope exchange of methylmercury bromide with mercury bromide by a factor of only 1.8.

However, the effect caused by the addition of bromide ions is fundamentally different from the usual salt effect, and may be regarded as catalytic. For example, the addition of an equimolecular concentration of  $\text{LiBr}$  to the system  $\text{MeHgBr}-\text{HgBr}_2-\text{EtOH}$  resulted in almost hundredfold acceleration.

The specific action of the alkali metal halides is evidently due to the ability of halogen ions to coordinate to the mercury. According to the author's hypothesis, complexes of two types— $\text{HgX}_3^-$  and  $\text{RHgX}_2^-$ —take part in the reaction and in the arising transition state the halogen anions form a "bridge" between two  $\text{Hg}$  atoms. Depending on the relative concentration of the exchanging reactants and the catalyst halide salt, the reaction mixture will contain only  $\text{HgX}_3^-$  or both  $\text{HgX}_3^-$  and  $\text{RHgX}_2^-$ , and either one or two anions will be present in the transition state. On the basis of this, the authors put

forward the idea of one-anion and two-anion catalysis<sup>16-19</sup> (see also Ref. 7).

Under the conditions of one-anion catalysis the transition state is formed by a molecule of the organomercury compound and the anion  $\text{HgX}_3^-$  (structure I), the bromine forming a linkage between two atoms of  $\text{Hg}$ . In two-anion catalysis the transition state consists of two anions,  $\text{HgX}_3^-$  and  $\text{RHgX}_2^-$  (structure II), again with bromine forming a bridge between the  $\text{Hg}$  atoms.



In the authors's opinion, the halogen anions are bound more strongly in the transition state than in the starting reactants, because they are held not by one but by two atoms of  $\text{Hg}$ . As a result of a gain in energy due to the formation of a cyclic transition state under catalytic conditions, the rate of the isotope exchange is sharply increased.

However, this argument does not exclude the possibility of a second hypothesis, namely that the reaction is accelerated owing to a considerable polarization of  $\text{C}-\text{Hg}$  and  $\text{Hg}-\text{Br}$  bonds, which increases the nucleophilic character of the substrate and the tendency of the electrophilic reagent towards nucleophilic coordination.

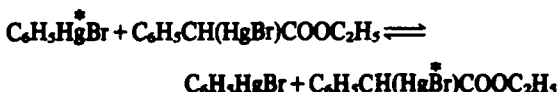
### 3.1 Two-alkyl exchanges

Exchanges between two organomercuries, of the type:



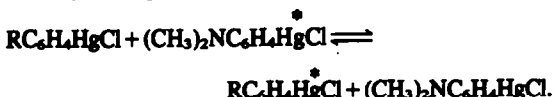
have so far been studied in a limited number of examples.

Thus Reutov *et al.*<sup>20</sup> reported some results on the exchange of <sup>203</sup>Hg-labelled phenylmercury bromide with ethyl  $\alpha$ -bromomercuriphenylacetate in pyridine:



The reaction is of overall second order (first order with respect to each component), with  $K_2 = 4.4 \times 10^{-3}$  l/mole sec at 40°. The activation energy is 12 kcal/mole.

Another example of this type of reaction is the exchange between phenylmercury chloride and *p*-dimethylaminophenylmercury chloride in toluene at 30°.



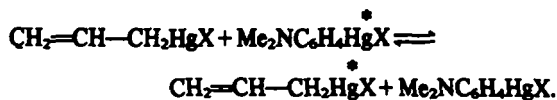
The overall order is equal to 2, but the partial orders on each reactant are fractional, indicating a complex character of the reaction. It should be noted that *p*-dimethylaminophenylmercury chloride is very unstable and decomposes spontaneously at a fairly rapid rate with liberation of metallic mercury.

The nature of substituent in the *para* position of the benzene ring in phenylmercury chloride has a strong influence on the reaction rate. Thus if the substituent is a

OMe group the equilibrium is established within an hour, while in the case of the ethoxycarbonylsubstituted compound the exchange proceeds to the extent of only 3% after 6 hr. The effect of the substituents R on the rate of exchange decreases in the order:

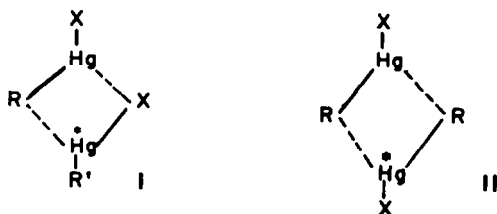


The nature of the anion was found to have a strong influence: thus the half-period of the exchange was 320 min for the chlorides at 70°, and in the case of the acetates the equilibrium was complete after less than 5 min at 20°. When the phenylmercury halide was replaced by allylmercury halide, the isotopic equilibrium was established almost instantaneously.<sup>21</sup>



No other reports have as yet appeared on this type of isotope exchange, probably owing mainly to the appreciable difficulties in separation of the reactants. The reactions studied involved organomercury compounds the separation of which presented no particular difficulties.

Two-alkyl exchanges are interesting from the point of view of the structure of the transition state. If we assume that a closed 4-membered transition state appears in a bimolecular reaction, we must choose between structures I and II

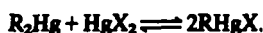


Structure I, in which the halogen is coordinated to the Hg atom, and which is postulated for one-alkyl exchanges, does not lead to the products of the exchange. If, however, we assume a transition state with an alkyl bridge (coordination R→Hg) we should expect reactions of this type to occur with greater difficulty than one-alkyl and three-alkyl exchanges. This problem must be studied for a series of related compounds, i.e. we must compare, for example, the rates of exchange in systems  $\text{RHgX}-\text{R}'\text{HgX}$  and  $\text{R}_2\text{Hg}-\text{RHgX}$ .

The two-alkyl exchanges include also the symmetrization of organomercury compounds,



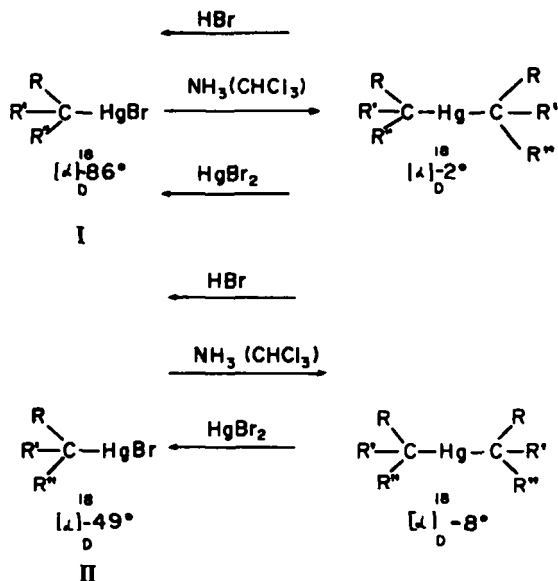
and the reverse reactions (disproportionations):



**3.1.1 Symmetrizations of organomercury compounds.** The symmetrization of organomercury salts under the influence of ammonia was the first  $\text{S}_{\text{N}}2$  reaction to be subjected to simultaneous kinetic and stereochemical studies.<sup>22-25</sup>



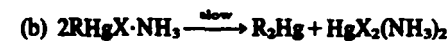
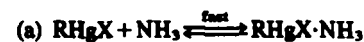
The stereochemistry was studied on the symmetrization of diastereoisomeric 1-methyl  $\alpha$ -bromomercuriphenylacetates with ammonia in chloroform.<sup>22</sup> In the symmetrization of diastereoisomer (I) with  $[\alpha]_{\text{D}}^{18} = -86^\circ$  the product is the only isomer of the symmetrical organomercury compound characterized by  $[\alpha]_{\text{D}}^{18} = -2^\circ$ , which is reconverted into the original diastereoisomer in the presence of an equimolecular amount of HBr or  $\text{HgBr}_2$ . The symmetrization of diastereoisomer (II), characterized by  $[\alpha]_{\text{D}}^{18} = -49^\circ$ , leads to another—and again the only possible one—symmetrical organomercury compound with  $[\alpha]_{\text{D}}^{18} = -8^\circ$ , which is reconverted into the original diastereoisomer (II) under influence of HBr or  $\text{HgBr}_2$ .



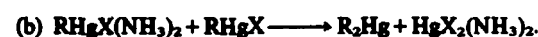
These results show that symmetrization of organomercury salts which represent electrophilic substitution at a saturated C atom, proceeds with retention of the configuration. It may also be concluded that the reverse reaction, i.e. the reaction of symmetrical organomercury compounds with mercuric halides, similarly proceeds with retention of configuration.

Kinetics of symmetrization were studied in the case of ethyl and 1-menthyl  $\alpha$ -bromomercuriphenylacetates by a method based on nephelometry. It has been found that the reaction reaches completion (in chloroform at 20°) only in the presence of a large excess of ammonia (at least a tenfold excess), and is of second order with respect to both the organomercury salt and ammonia.<sup>25</sup>

The kinetic and stereochemical results obtained in studying the symmetrization of ethyl  $\alpha$ -bromomercuriarylacates under the influence of ammonia thus agree best with one of the two schemes:<sup>26-28</sup>



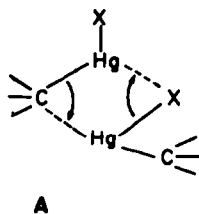
Scheme 1.



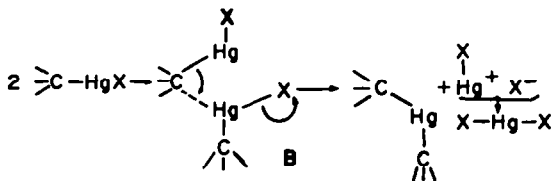
Scheme 2.

In both schemes the step (b) is  $S_N2$  reaction.

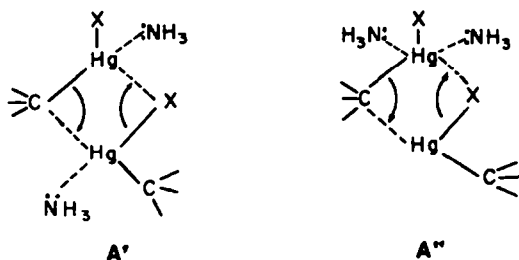
There is no experimental evidence on which to base a choice between these two possibilities; both may in fact occur together. It is easy to see, however, that the transition state should in both cases by a 4-membered ring of type A:<sup>24</sup>



This transition state is proposed on the following basis. The reaction is bimolecular (of first order with respect to each component and of overall second order) and proceeds with strict retention of the configuration (the incoming metal acquires the position of the leaving atom). The open transition state of type B is not very probable in solvents of low polarity (chloroform) because it would lead to the intermediate ions  $X^-$  and  $HgX^+$  (or rather  $NH_3HgX^+$  or  $(NH_3)_2HgX^+$ ).



The only difference between the transition states in Schemes 1 and 2 is that, in the first one (A') both atoms are coordinated to molecules of  $NH_3$ , while in the second case (A''), one of the Hg atoms is coordinated to two ammonia molecules:



Since the transition states A' and A'' do not differ essentially from the transition state A, the general conclusions reached in examining A and without taking into account the solvation and the coordination of the Hg

atoms will be identical.<sup>25</sup> The 4-membered cyclic transition state A will therefore be used for simplification in further discussion ("in the pure state"), but it should always be borne in mind that either one or both Hg atoms are solvated by ammonia molecules.

To study the effect of structural factors on the rate of symmetrization, the authors used numerous ethyl  $\alpha$ -bromomercurylacetates with various electron-acceptor and electron-donor substituents in the *ortho*-, *meta*- and *para*-positions of the benzene ring.<sup>29-32</sup> The effect of substituents in various positions was thus evaluated in order to resolve their polar effect into components (inductive effect and effect of conjugation). A further aim was to elucidate the possibility of hyperconjugation in the given system.

The values thus obtained for the second-order rate constants of symmetrizations are listed in Table 3.

These rate constants show that the nature of the substituents Y exerts a very strong influence on the rate of symmetrization. Electron-acceptors ( $NO_2$ , Hal) accelerate and electron-donors (Alk) retard the reaction. With Y =  $NO_2$  the reaction was so fast that its rate could not be measured. The substituent effect obeys Hammett's equation (Fig. 1) with  $\rho = 2.85$ .<sup>33</sup>

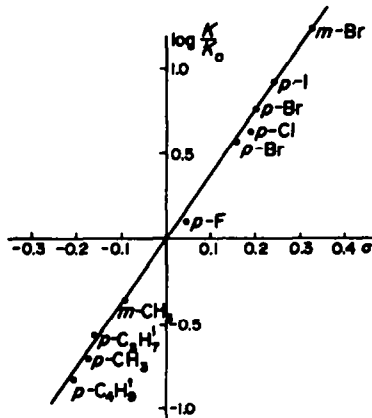


Fig. 1. Application of Hammett's equation to kinetics of symmetrization of  $p$ - $YC_6H_4CH(HgBr)COOC_2H_5$ .

It should be noted that the effect of substituents in this bimolecular reaction is anomalous from the viewpoint of an  $S_N2$  mechanism, and agrees instead with an  $S_N1$  mechanism. A similar relationship was later found in the protolysis of alkylmercury iodides.<sup>33</sup>

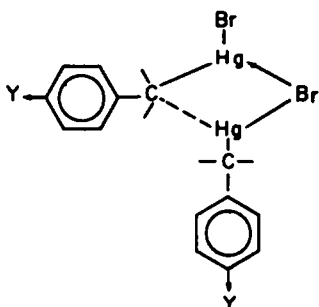
These facts have been explained initially in such a way that even in bimolecular substitutions, it is the rupture of the old bond and not the formation of the new one that may play the important part.<sup>31-33</sup> By the way, it must

Table 3. Rate constants of symmetrizations

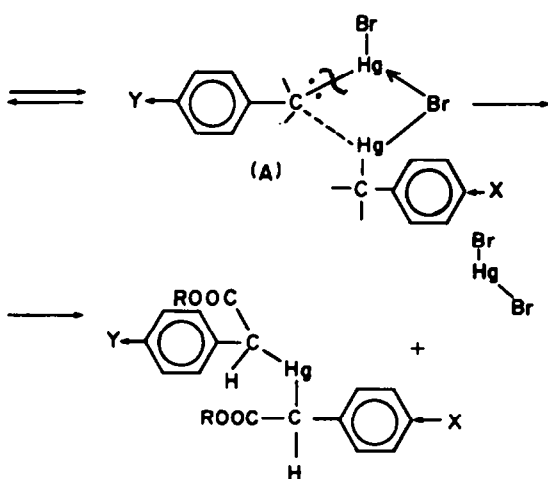
Y	<i>p</i> -NO <sub>2</sub>	<i>p</i> -I	<i>p</i> -Br	<i>m</i> -Br	<i>o</i> -Br	<i>p</i> -Cl	<i>p</i> -F	H
$K_2 \times 10$ (l/mole sec)	Very fast (177.3)†	6.7	5.4	14.45	4.26	4.7	1.48	1.1
Y	<i>p</i> -CH <sub>3</sub>	<i>m</i> -CH <sub>3</sub>	<i>o</i> -CH <sub>3</sub>	<i>p</i> -C <sub>2</sub> H <sub>5</sub>	<i>p</i> - <i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub>		
$K_2 \times 10$ (l/mole sec)	0.34	0.71	0.407	0.32	0.417	0.28		

†The rate constant was calculated by applying Hammett's equation to the series of reactions.

therefore be assumed that not only the rupture of the C-Hg bond, but also the coordination of bromine to mercury is important in transition state (explanation at present see Section 8).



Owing to the structure of this transition state, the substituent Y plays a twofold part: thus, when it promotes rupture of the C-Hg bond on the one hand, it simultaneously hampers the rupture of the Hg-Br bond on the other, i.e. hinders the coordination of bromine of the second molecule with mercury, and *vice versa*. The best situation is therefore reached in the "co-symmetrization" of such differently substituted mercurated esters  $YC_6H_4CH(HgBr)COOEt$  and  $YC_6H_4CH(HgBr)COOEt$ , in which the substituents X and Y exert very different polar effects. This is because in this case each substituent can fulfil a function that is most favourable for the reaction. It has in fact been shown that the rate of such reactions always exceeds even that of the symmetrization of the fastest reaction component.



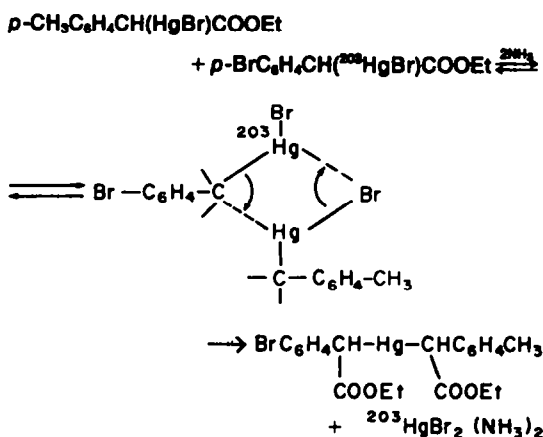
This type of "co-symmetrization" has been carried out with Y and X being Br and H, H and Me, and Br and Me.<sup>33</sup>

Experiments with symmetrization of a mixture of two differently substituted organomercury compounds, one of which was labelled with  $^{203}Hg$ , confirmed the assumption that the rupture of the C-Hg bond in co-symmetrization proceeds in the molecule with an electron-acceptor substituent.

If co-symmetrization indeed proceeds via transition

state A then the co-symmetrization of two salts, one of which is labelled with mercury, is expected to show no statistical distribution of the activity between the resulting  $RHgR'$  and  $HgBr_2(NH_3)_2$ . In fact, the activity was predominantly (80%) exhibited by the second species in the co-symmetrization of *p*-bromo-substituted and *p*-methyl-substituted ethyl  $\alpha$ -bromomercuriphenylacetates, the first of which was labelled with  $^{203}Hg$ .

The presence of activity in the precipitate may be merely the result of rupture of the C-Hg bond in ethyl  $\alpha$ -bromomercuri-*p*-bromophenylacetate. This means that the reaction occurs according to the following schemes:

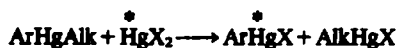


On the other hand, if the labelled atom is in the molecule with the electron-donor substituent, as in the co-symmetrization of *p*-*i*- $C_3H_7-C_6H_4CH(^{203}HgBr)COOEt$  and *p*- $BrC_6H_4CH(HgBr)COOEt$ , then the activity remains predominantly (70.5%) in  $RHgR'$ . Therefore, the character of the cleavage of the C-Hg and Hg-Br bonds in the transition state A depending on the electronic character of the substituents X and Y can be regarded as established.

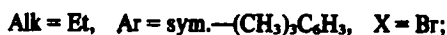
**3.1.2 Disproportionations of organomercury compounds.** The mechanism of disproportionations of organomercury compounds  $R_2Hg + HgX_2 \rightarrow 2RHgX$  has been studied by several authors.<sup>35-38</sup>

In all cases the disproportionations proceed as  $S_E2$  reactions with retention of configuration. In two cases the results were not in agreement with  $S_E2i$  mechanism.<sup>39,40</sup> The distribution of the activity between  $C_6H_5HgCl$  and  $C_2H_5HgCl$  molecules, determined by the use of labelled  $HgCl_2$ , was found to be uniform (50:50). This anomaly was explained by a non-linear structure of organomercury compounds, which makes possible the formation of a 6-membered transition state in which the two Hg atoms are equivalent.<sup>39</sup> It has been found in similar experiments<sup>40</sup> on the disproportionation of *n*-butylphenylmercury with labelled mercuric bromide that all the activity is transferred to the butylmercury bromide.

However, a repeat of these investigations<sup>41</sup> revealed that the reaction between arylalkylmercury and labelled mercuric halide leads to the formation of inactive alkylmercury halide and active arylmercury halide carrying all the activity:



where



The results of this work are in complete agreement with the position of these groups in Kharasch's electronegativity series, and make it unnecessary to search for a new mechanism (more complicated than  $S_N2i$ ) of electrophilic substitution at the saturated C atom.

#### 4.1 Three alkyl exchanges

An example of a 3-alkyl exchange is the reaction between organomercuries and organomercury salts. These reactions may be used to prepare unsymmetrical organomercury compounds  $\text{R}'\text{HgR}$ .<sup>42</sup>

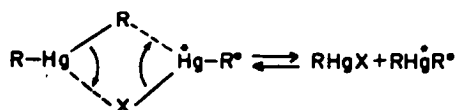


The 3-alkyl isotope exchange has so far been studied only with organomercury compounds containing the same radicals.<sup>43-45</sup> The first work on the mechanism of the 3-alkyl isotope exchanges was concerned with the exchange between bis-(2-methylhexyl-5)-mercury and 2-methylhexyl-5-mercury bromide in absolute ethanol at 60°. The authors used simultaneously two "labels": an isotopic label (mercury) and a stereochemical label (the alkyl radical). Thus the rate of the process could be observed by the transition of each label:



The investigations showed that this reaction proceeds with strict retention of configuration. The reaction is accompanied by distribution of the optical activity between  $\text{RHgX}$  and  $\text{R}_2\text{Hg}$ , and the rate of exchange of the optically active for the inactive radical is the same as the rate of exchange of the labelled Hg atom for the inactive one.

The mechanism represented by the next scheme agrees with the experimental data:



Kinetic studies<sup>44</sup> of this reaction have shown that the process is of overall second order, being of first order with respect to each component

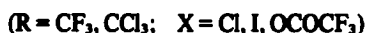
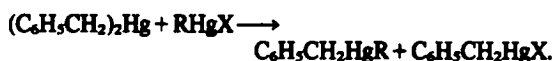
$$(k_2^{60^\circ} = 1.33 \text{ l/mole h}; \\ E = 15.3 \text{ kcal/mole}; \Delta S^\ddagger = -31.6 \text{ e.u.}).$$

An analogous reaction has been investigated by Ingold *et al.*<sup>45</sup> also by the double-label method, ( $\text{R} = \text{sec-Bu}$ ). Kinetic and stereochemical studies of the reaction in ethanol led to the same results as those obtained with  $\text{R} = 2\text{-methylhexyl}$ .

3-Alkyl exchange is a form of electrophilic substitu-

tion; it is bimolecular and proceeds with retention of the configuration. The problem of choosing between  $S_N2$  and  $S_N2i$  mechanism has been solved differently by the two groups of workers for organomercury halides. In the view of Ingold *et al.* definite preference is given to an open transition state. The arguments in favor of this structure are the increase in the rate with increasing ionic character of the  $\text{Hg-X}$  bond, and the considerable positive salt effect, indicating that the transition state is more polar than the initial state.

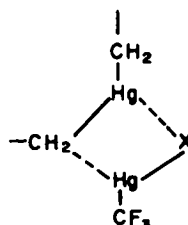
On other hand in some cases of 3-alkyl exchanges definite preference should be given to a closed transition state. Reaction of dibenzylmercury with organomercury salts<sup>46</sup>



has second order in overall and first in respect to each component.

The values of  $K_2$  of these reactions are listed in Table 4.

These rate constants show that the rate of reaction depends not only on the electrophilicity of mercury in  $\text{CF}_3\text{HgX}$  but also on the nucleophilicity of X, i.e. the transition state of the reaction (at least for  $\text{X} = \text{I}$  and  $\text{X} = \text{OCOCF}_3$ ) has a cyclic structure



#### 5.1 Four-alkyl exchanges

In the first work on an isotope exchange of this type



it appears that the reaction proceeds under mild conditions.<sup>47</sup> Thus, in the reaction of diphenylmercury and di-*p*-anisylmercury with mercury-bis-acetaldehyde, the isotopic equilibrium in acetone at room temperature is established almost instantaneously.

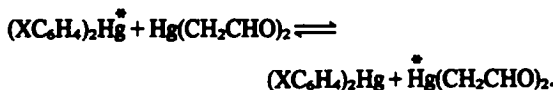


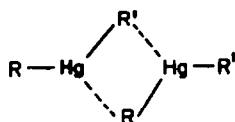
Table 4. Rate constants ( $K_2 \times 10^3 \text{ l/mol sec}$  at 31°) of reaction  $\text{Bz}_2\text{Hg} + \text{CF}_3\text{HgX}$  in different solvents

Solvent	Rate constants		
	$\text{CF}_3\text{HgOCOCF}_3$	$\text{CF}_3\text{HgI}$	$\text{CF}_3\text{HgCl}$
Tetrachloroethylene	720	2.10	1.70
Dichloromethane	53.7	0.062	0.035
DMS	61.2	0.062	0.032
DMF	59.8	0.119	0.023
Acetone	39.4	0.066	0.0086
Benzene	11.4	0.042	0.0065
Pyridine	0.65	0.002	0.0005



Isotope exchange has been observed between diphenylmercury and di-*p*-chlorophenylmercury in pyridine at 60°. The authors believe that this is not a free radical reaction, since organomercury compounds probably do not form any free radicals under these conditions.

In the course of general study of exchanges in systems  $R_2M-R_2M$  Dessy *et al.*<sup>48</sup> established that by heating for a long time at 65° in the system  $(CH_3)_2Hg-(CD_3)_2Hg$  the unsymmetrical compound  $CD_3HgCH_3$  appears in the reaction mixture. On this basis the preference was given to a 4-membered cycle transition state compared with octahedral transition state.



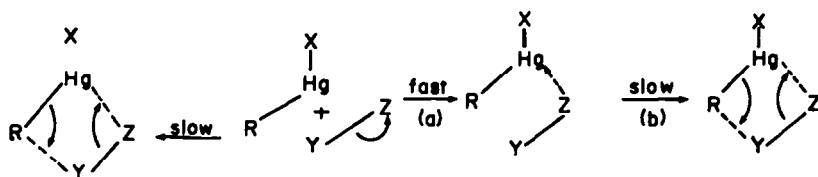
Recently an approach was developed which allows to rationalize the structure effects on positions of redistribution equilibria in different types of exchange reactions of organometallic compounds (including 4-alkyl exchanges). The approach is based on the comparison of relative stabilities of anions corresponding to exchanging groups and complexochemical properties of organometallic cations in which exchange occurs<sup>110a</sup> (see also Section 8.1).

### 6.1 Stereochemistry of bimolecular electrophilic substitution ( $S_{E2}$ rule)

In all cases of bimolecular electrophilic substitution which have been studied<sup>16-18,22,49,53,54</sup> (1-alkyl, 2-alkyl and 3-alkyl exchanges) the strict retention of configuration at saturated carbon was established.†

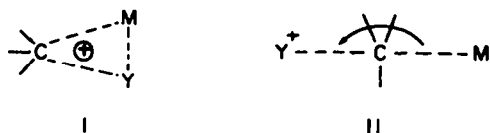
The question is: why retention always observed?

In the case of  $S_{E2}$  mechanism a retention of configuration is predestined by coordination of nucleophile Z with the Hg atom in one- or two-step reactions:



In the case of an open transition state ( $S_{E2}$ ) the reasons also exist for preference of retention of configuration.

In the case of two possible transition states, I (with retention) and II (with inversion) it will be concluded that



the transition state I should be more stable.<sup>57,58</sup> In this transition state we have a cyclic system consisting of a three nucleus and two electrons. As it is known, such a

†The only case of inversion of configuration observed for bromination of *S*-(+)-sec- $C_4H_9Sn$ (neopentyl)<sub>3</sub><sup>55</sup> was found to be due to the steric effect of the leaving group.<sup>56</sup>

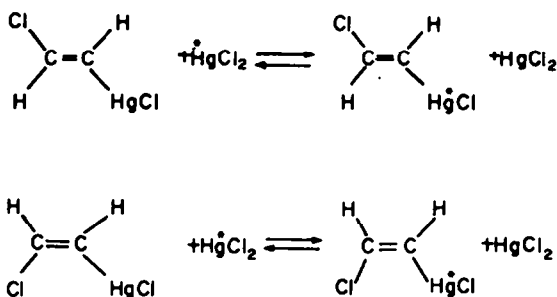
system really exists in some ions, for instance in  $H_3^+$  and  $CH_5^+$ .

Thus the  $S_{E2}$  reactions at saturated C atoms occur with retention of stereochemical configuration ( $S_{E2}$  rule).<sup>59</sup> The  $S_{E2}$  rule applies not only to closed transition states ( $S_{E2i}$ ) but also to open transition states.

### 6.2 Bimolecular electrophilic substitution at olefinic carbon of organometallic compounds

Among the three possible types of substitution at an olefinic C atom the greatest attention from the point of view of stereochemistry has been devoted to electrophilic and homolytic substitutions. Starting with *cis*- and *trans*- $\beta$ -chlorovinyl organomercury compounds with rigorously established configuration, Neameyanov and Borisov studied the stereochemistry of numerous transitions of chlorovinyl radicals from one metal to another<sup>60</sup> and finally formulated a rule according to which the geometrical configuration is preserved in electrophilic and radical substitutions at an olefinic carbon.

The stereochemistry of one-alkyl electrophilic substitution at an olefinic carbon was studied in the isotope exchanges between *cis*- and *trans*- $\beta$ -chlorovinylmercury chlorides with radioactive mercuric chloride,<sup>5</sup> in acetone at room temperature. In both cases the isotope equilibrium became established in less than 5 min, and the geometrical configuration was strictly retained.

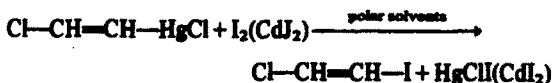


Since the fast exchange did not permit a study of the kinetics, the authors had insufficient grounds for formulating its mechanism. However, the absence of bis- $\beta$ -chlorovinylmercury in the reaction mixture shows that the exchange is due to a direct interaction between the  $\beta$ -chlorovinylmercury chlorides and the mercuric chlorides, so that the results are a direct confirmation of the rule that the configuration at an olefinic carbon is retained in electrophilic substitution.

The model reaction chosen for simultaneous kinetic and stereochemical studies was the cleavage of the C-Hg bond in isomers of  $\beta$ -chlorovinylmercury chloride and styrylmercury bromide under the action of iodine and bromine.<sup>61-64</sup>

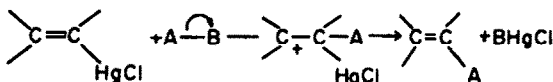
The authors were able to conduct these reactions by various mechanisms—electrophilic (mono- and bimolecular) and free-radical—and to study the kinetics and the stereochemistry under these conditions. The investigations were carried out in a number of polar

solvents (aqueous dioxan, DMF, methanol) in the presence of  $\text{CdI}_2$  in the case of iodine and  $\text{NH}_4\text{Br}$  in the case of bromine and later also in nonpolar solvents—benzene, carbon tetrachloride.

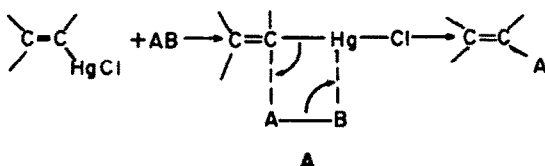


The kinetics were followed spectrophotometrically at various temperatures and various starting concentrations of the reactants, in the presence of a tenfold excess of the halide anion. Under these conditions the reaction in all solvents was second order and had first partial order.<sup>61</sup> The reaction proceeds with strict retention of the geometrical configuration.

On the basis of stereochemical and kinetic data an attempt can be made to formulate some ideas about the mechanism of the studied reactions. It may be said that the electrophilic reactions do not proceed via an intermediate formation of a carbonium ion since the starting geometrical configuration would then be lost.



The participation of the  $\text{I}_3^-$  anion in the iodination indicates that the reaction takes place through a transition state of type A without intermediate formation of a  $\pi$  complex between the halogen and the olefin:



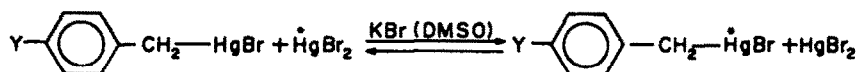
The formation of the final product through a cyclic 4-membered transition state occurs with retention of the configuration similar to other  $\text{S}_{\text{N}}2$  reactions.

This mechanism is in agreement with the fact that the solvents exert the same effect on the reaction of iodine in the presence of iodine ions in the case of benzylmercury chloride and in the case of  $\beta$ -chlorovinylmercury chloride.

#### 7. NUCLEOPHILIC CATALYSIS IN $\text{S}_{\text{N}}2$ REACTIONS

The added complexing agent (anions or neutral molecules) can increase the rates of  $\text{S}_{\text{N}}2$  reactions of organometallic compounds by several powers of ten.

Nucleophilic catalysis was studied in detail using one-alkyl isotope exchange reaction of benzylmercuric bromides with  $\text{HgBr}_2$  in DMSO as a model.<sup>62</sup> The reaction was found to be strongly catalysed by anions (such as halide ions) which are known to coordinate with mercuric salts. The catalysed reaction is generally of the form:



In the solvent dimethylsulphoxide, second order kinetics are observed.

The acceleration in rate produced by added bromide ions shows that the reaction is still an independent process, and not a combination of two steps of the 2-alkyl exchange, since the 2-alkyl exchange is known to be strongly retarded by halide ions.<sup>66</sup>

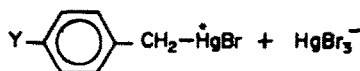
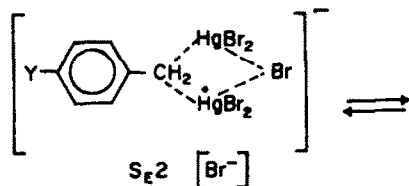
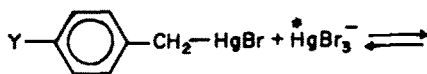
The magnitude of the catalysis can be for instance illustrated by the following data:<sup>65</sup>

$[\text{KBr}]$ , mole $\text{l}^{-1}$	0	0.06	0.12	0.18
$10^2 K_2$ , $\text{l mole}^{-1} \text{h}^{-1}$	37	148	1444	2139

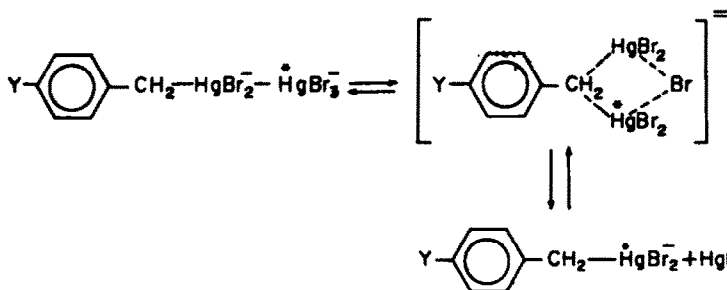
If the two reactant concentrations are kept constant ( $[\text{RHgBr}] = [\text{HgBr}_2] = 0.06$ ), then the second order rate constant,  $K_2$ , increases linearly with increasing bromine ion concentration  $[\text{Br}^-]$  up to the point where  $[\text{Br}^-] = 0.06$ . At this point there is a sharp change in gradient, although the relationship between  $[\text{Br}^-]$  and  $K_2$  continues to be linear. This change at  $[\text{Br}^-] = 0.06$  indicates that two types of catalysis are operative. No further change in gradient is observed at  $[\text{Br}^-] = 2 \times 0.06$ .

The observed catalysis is too large to be explained in terms of a normal salt effect; it indicates the incursion of a new mechanism in which one or more of the added bromide ions are involved in the rate-determining step. At low concentrations of the added anion ( $[\text{Br}^-] < 0.06$ ), only one anion is involved in the rate-determining step. These two forms of catalysis are distinguishable kinetically, and have been called by Ingold as the "one-anion" and "two-anion" catalysed reactions.<sup>17</sup>

It is usually believed that the bromide anion complexes strongly with  $\text{HgBr}_2$ , but only very weakly with  $\text{RHgBr}$ . For the reaction under study, however, the halide ion complexes strongly with  $\text{HgX}_2$  in the initial state, but even more strongly in the transition state where it acts as a bridge between a partially formed  $\text{HgX}_2$  molecule and a partially formed  $\text{HgX}_3^-$  ion. The overall result is a larger increase in rate.

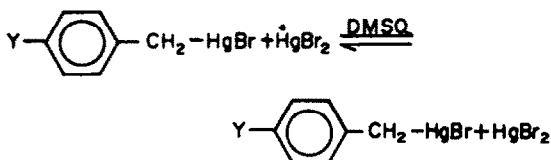


When the concentration of added anion exceeds the reactant concentration ( $[\text{Br}^-] > 0.06$ ), a second anion is involved in the rate-determining step. The suggested transition state for this "two-anion" catalysed reaction is shown on the following page.

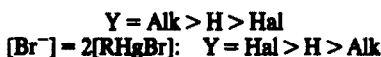


In the reaction under study the two-anion catalysis is stronger than the one-anion catalysis.†

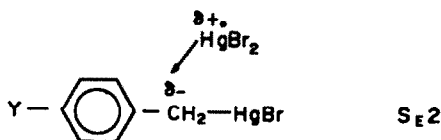
The influence of the substituents Y on the rate of the non-catalysed reaction and of the two-anion catalysed reaction is different:



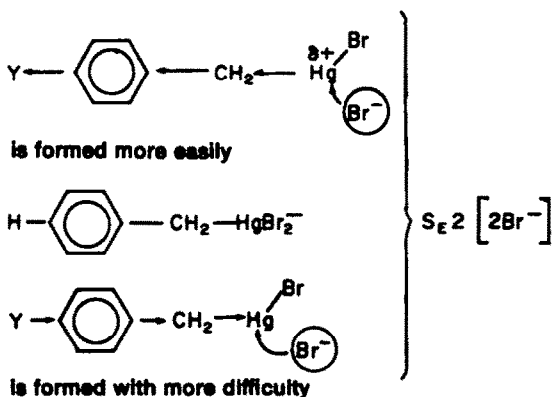
without  $[\text{Br}^-]$ :



This inversion in the influence of the substituents can be explained if we take into consideration that for the first reaction the value of  $\delta^-$  on the C atom is important

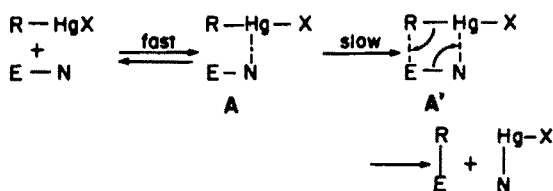


whereas for the two-anion catalysed reaction the ease of formation of the anion  $\text{RHgBr}_2^-$  is very important which depends on the value of  $\delta^+$  on the Hg atom:

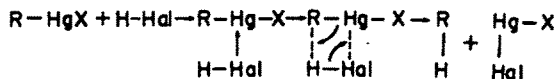


The work of some authors<sup>180-182</sup> has shown that in the reaction of organomercury compounds a role of considerable magnitude is played by the opportunity for internal catalysis or nucleophilic assistance, e.g. preli-

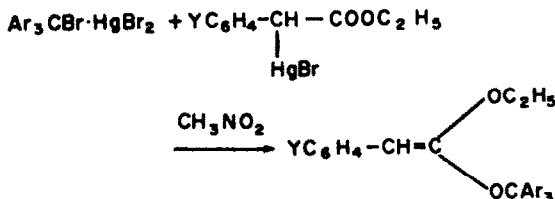
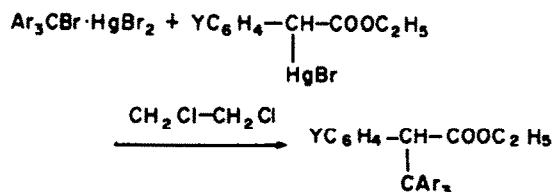
minary coordination of the Hg atom of the  $\text{RHgX}$  by the nucleophilic part of the reacting molecule EN (intermediate A). This results in the formation of a cyclic transition state (A') in which nucleophilic attack on the Hg atom and electrophilic attack on the C atom is carried out simultaneously by different parts of the attacking agent. It is also possible that the nucleophilic attack on the Hg atom precedes the rate-determining step.



The study of protolysis of organomercury compounds by HCl in organic solvents showed that the rate of reaction decreases with the increase in water content of solvents. This means that the reacting agent is a non-ionized molecule HCl.<sup>183,184</sup>

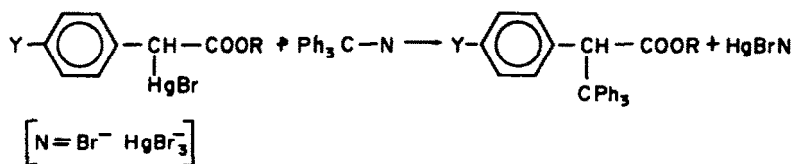


Reaction with  $\text{HClO}_4$  does not occur at all because of the absence of the tendency of  $\text{HClO}_4$  towards coordination with the Hg atom (nucleophilic assistance). The alkylation of organomercury compounds with triaryl-bromomethane was studied<sup>182</sup> taking into consideration the idea of nucleophilic assistance. It was previously shown,<sup>79</sup> that depending on the nature of the solvent the reaction of triphenylbromomethane and of its complex with mercuric bromide with the ethyl ester of  $\alpha$ -bromomercuriphenylacetic acid takes place either exclusively at the C atom (in dichloroethane) or practically exclusively at the O atom, i.e. with transfer of the reaction centre (in nitromethane):

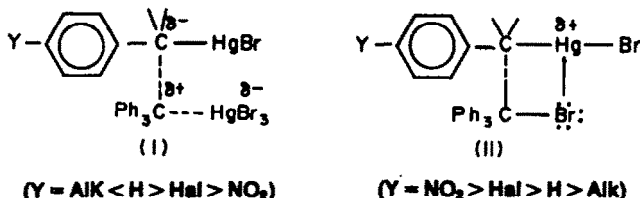


†In general, it is not possible to predict whether the two-anion catalysis is stronger or weaker than the one-anion catalysis. In fact both types of behavior are observed.<sup>67</sup>

Moreover, it was found that with either solvent, the addition of mercuric bromide to the reactants leads to a decrease in reaction rate.<sup>79</sup> It is known that complexes of alkyl halides with Lewis acids are more highly ionized and are stronger alkylating agents than are alkyl halides themselves. According to the data of Skoldinov and Kosheshkov,<sup>183</sup> organometallic compounds are no exception. Thus, alkylation and acylation of organomercury and organotin compounds are greatly facilitated by the presence of aluminium chloride. Therefore, the result showing that the reaction is inhibited by mercuric bromide is anomalous. In addition, it was found that the reaction does not generally take place in the presence of a stronger Lewis acid, such as stannic chloride, which forms the ionized compound  $[(C_6H_5)_3C^+ \cdot 2SnX_4^{2-}]$  with triphenylbromomethane. Negative results were also obtained when the completely ionized triphenylmethyl perchlorate was used.



Hence, it follows that transition states of different structures are formed with different alkylating agents, the cyclic structure (II) is formed in the case of triphenylbromomethane and the non-cyclic structure (I) results in the case of its complex with mercuric bromide (see Section 8).



amounts of complex, but only of differences in the strength of the bromine-mercury bond in the complexes. In this case, the rate-determining factor is apparently scission of the C-Hg bond, and the mechanism in this reaction is most probably S<sub>E</sub>1 (see Section 8). In any case, it is a fact that the effect of substituents changes under conditions favourable to nucleophilic coordination.

Since, however, the ethyl ester of  $\alpha$ -bromomercuriphenylacetic acid does not react with  $(C_6H_5)_3CBr \cdot SnCl_4$  or with  $(C_6H_5)_3CBr \cdot SnCl_4$ , it cannot be assumed that in the case of  $(C_6H_5)_3CBr \cdot HgBr_2$  transition state (I) represents an extreme case of a completely open system, since even an increase in the electrophilic properties of the reagent, under conditions such that coordination at the mercury does not occur at all does not make alkylation possible.

Different results were obtained in a study of the alkylation of an aromatic system, *viz.* phenylmercury

bromide.<sup>80</sup> In contrast to ethyl esters of  $\alpha$ -bromomercuriphenylacetic acids, phenylmercury bromide does not form a complex with triphenylbromomethane under these conditions, and, therefore, alkylation reactions with both reagents,  $(C_6H_5)_3CBr$  and  $(C_6H_5)_3CBr \cdot HgBr_2$ , are of the second order, while as in the case of the

These cases also differ kinetically. The reaction of the organomercury compound with the complex  $(C_6H_5)_3CBr \cdot HgBr_2$  is of the second order; in the case of tribromomethane itself, a complex with a molecule of the organomercury compound is formed before the rate-determining step, and this complex then reacts intramolecularly (see Section 8) in accord with a first order rate law.<sup>79</sup> The effect of substituents in the molecule of organomercury compound also differs in these two cases. In reactions of the complex  $(C_6H_5)_3CBr \cdot HgBr_2$  with substituted mercuriated esters, the order of the effect of substituents is that usually observed in electrophilic substitutions, specifically, electron-donor substituents promote the reaction, while electron-acceptor substituents retard.<sup>79</sup> The effect of substituents is completely reversed in reactions with triphenylbromomethane itself. It may be assumed that this fact is associated with the effect of the substituents on the strength of the Br→Hg coordination in the resulting complex. It should be mentioned that for all complexes formed, the optical density of the solutions (obtained by extrapolation of the kinetic curves  $d = f(\tau)$  to  $(\tau \rightarrow 0)$ ) is the same at different concentrations regardless of the nature of the substituent in the organomercury compound. Therefore, we may not speak of different

mercuriated ester, the reaction rate decreases on going to the complex. However, the possibility that this is due to the presence of excess mercuric bromide cannot be ignored, since it has previously been shown<sup>71</sup> that mercury bromide retards certain reactions of phenylmercury bromide, for example, protolysis. It may be presumed that the structure of the transition state is close to the non-cyclic structure in phenylmercury bromide reactions. This is confirmed by a study of the effect of structural factors. The effects of substituents in the phenylmercury bromide molecule on the reactions with triphenylbromomethane and its complex with mercuric bromide proved to be the same and characteristic of electrophilic substitutions. The assumption of a non-cyclic structure for the transition state in alkylation of phenylmercury bromide is also confirmed by the fact that in this case reaction also occurs under the influence of triphenylmethyl perchlorate. A rigorous kinetic study of the reaction is impossible, unfortunately, owing to the retarding effect of the mercuric bromide liberated. Thus, our results do not contradict the data reported,<sup>183</sup> although the fact that the ethyl ester of  $\alpha$ -bromomercuriphenyl acetic acid and phenylmercury bromide behave differently naturally requires explanation.

The inhibiting effect of mercuric bromide in reactions of phenylmercury bromide is removed by the addition of an excess of tetrabutylammonium iodide to the reaction mixture. In this case, the reaction rate is sharply increased (by a factor of  $\sim 10^3$ ), which as shown previously,<sup>51</sup> is apparently associated with the formation of the complex  $C_6H_5HgBrI^-$ . This may be considered as an example of nucleophilic assistance. However, a further increase in iodide concentration with respect to concentrations of the reagents (on going from 1:10 to 1:20) leads to a slight, but appreciable decrease in the rate of the reaction. An analogous but more substantial decrease in reaction rate in two-anion catalysis (i.e. under conditions such that the formation of a complex with a charge of two is possible) has been observed recently in other reactions, and has been explained by hindrance to nucleophilic assistance by the nucleophilic portion of the molecule at the four-coordinated mercury. The slight effect observed in the present case apparently suggests that if nucleophilic coordination does exist, it is slight; however, its complete absence cannot be assumed.

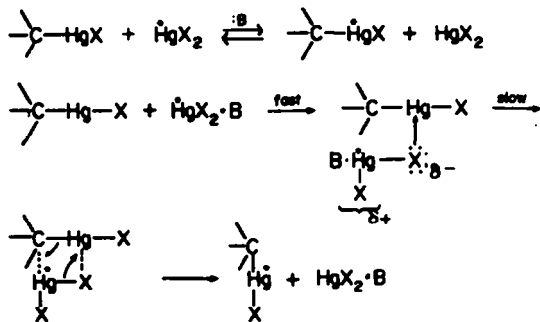
Whether it is possible for an electrophilic substitution to occur in an organomercury compound depends on a number of factors. With respect to the molecule of the organomercury compound, one such factor is polarization of the Hg-C bond, i.e. primarily the presence of an effective positive charge on the Hg atom, which determines whether nucleophilic assistance is possible. A no less important factor is electronegativity of the radical at which the electrophilic attack is carried out. In the molecule of the attacking agent, another factor is the magnitude of the effective positive charge on the C atom and of the effective negative charge on Br atom. Data on the effect of substituents in the molecule of the attacking agent illustrate the importance of both the nucleophilic attack on the Hg atom and the electrophilic attack on the C atom in alkylation reactions. On the one hand, tri(*p*-nitrophenyl)bromomethane, in which the C-Br bond is covalent so that nucleophilic assistance cannot occur, cannot generally be used as the alkylation agent (*p*-ethyl-, *p*-nitro-, and unsubstituted ethyl ethers of  $\alpha$ -bromomercuriphenylacetic acid, benzylmercury bromide, and *p*-tolylmercury bromide do not react). On the other hand, a decrease in the electrophilicity of the alkylating agent leads to a decrease in the reaction rate, even under conditions such that there is some increase in nucleophilic coordination. Thus, the rate of the reaction with mercuriated esters decreases on going from triphenylbromomethane to tri-*p*-tolylbromomethane.

Thus, the necessity of nucleophilic coordination is not the sole requirement in a number of cases. Apparently, an optimum situation is necessary: sufficient positive charge on the C atom constituting the electrophilic portion of the molecule and the possibility of nucleophilic assistance by the nucleophilic portion of the molecule. These requirements are not satisfied by either a covalent or a completely ionized alkylating compound, but only by a compound with a bond of a certain specific degree of ionic character.

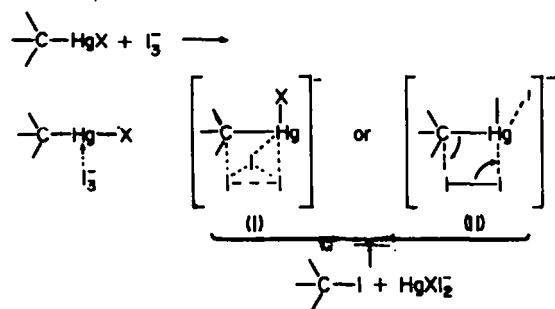
Using the idea of the nucleophilic assistance it is possible to explain many peculiarities of  $S_N$ -reactions.

For instance from this point of view the reactions in which acceleration of isotope exchange by means of bases has been observed can be explained by the next scheme including nucleophilic assistance.

The unusual  $S_N$ -reactions of the organomercury

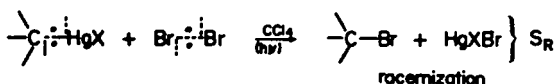


compounds under action of nucleophilic reagent  $I_3^-$  are now easy to understand taking into consideration the necessity of nucleophilic assistance:

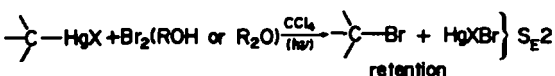


Use of nucleophilic catalysis may change the reaction mechanism; thus, it was shown that the reactions of  $RHgX$  with iodine or bromine proceed by a homolytic mechanism, but the mechanism changes to  $S_N2$  in the presence of some anions or neutral nucleophiles.

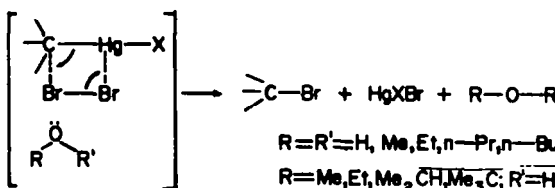
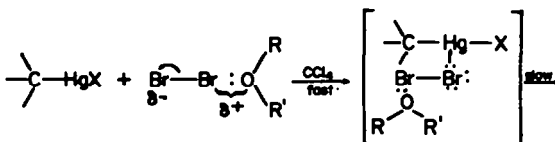
For instance the bromodemercuration reaction in carbon tetrachloride solution in day light proceeds as a  $S_N$ -reaction with formation of racemic alkyl halide.<sup>52</sup>



In the presence of ROH or  $R_2O$  this reaction becomes  $S_N2$  and proceeds with strict retention of configuration.<sup>53</sup>



Taking into consideration the hypothesis of nucleophilic assistance it is possible to explain this change of the mechanism because of a greater ability of complexes like  $\text{Br}_2 \cdot \text{OR}_2$  to nucleophilic assistance compared to that of  $\text{Br}_2$ :



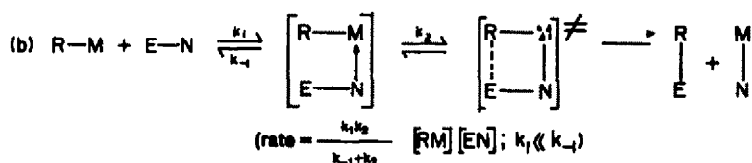
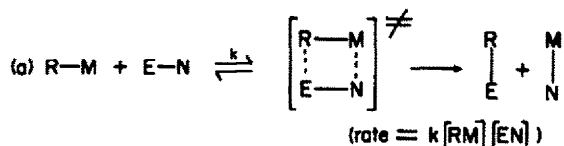
Since in organometallic reactions of the  $S_R$  type the role of the electrophile can be played by negatively charged entities ( $I_3^-$ ,  $HgBr_3^-$ , etc) one may conclude that (1) the controlling factor is not the electrophilicity of the electrophilic agent, but its ability to enter into nucleophilic coordination with the metal atom, and (2) electrophilic attack on a C atom proceeds only after nucleophilic coordination.<sup>6,70</sup>

Nucleophilic catalysis has opened some new synthetic pathways in organometallic chemistry. Thus, change from the stronger electrophilic  $Ph_3CClO_4$  to the weaker electrophile  $Ph_3CBr$ , which is capable of nucleophilic coordination, enables alkylations to be carried out with a series of organomercury compounds.<sup>71,72</sup> The catalytic reaction of organomercury compounds with acyl halides is a convenient method for synthesis of unsymmetrical ketones.<sup>73</sup> The reactions of  $RHgX$  or  $R_2Hg$  ( $R = C_6F_5$ ,  $MeCOCH_2$ ,  $(CF_3)_2CH$ ,  $CCl_3$ ,  $PhCHCOOEt$ ) with trinitrobenzene in the presence of  $I^-$ , or of  $R_3SnMe_3$  ( $R = MeCOCH_2$ ,  $PhC\equiv C$ ,  $cyclo-C_3H_5$ ,  $C_6H_5$ , etc.) in DMSO (which act as nucleophilic catalysts) result in quantitative yields of Meisenheimer's complexes  $C_6H_3(NO_2)_3R^-$ .<sup>74</sup>

### 8. $S_{R1}(N)$ MECHANISM IN ORGANIC CHEMISTRY

The majority of electrophilic substitution reactions in organometallic compounds have an  $S_{R2}$  mechanism, with attack of the electrophile at the metal bonded C atom being the most important reaction step. However, coordination of the nucleophilic part (N) of an electrophilic agent (E-N) with the metal atom is quite significant in such reactions, and this coordination on occasions has an important influence on the possibility of their occurrence. Such coordination is responsible for multicenter, e.g. four-center, transition states ( $S_{R2i}$  mechanism).

Nucleophilic coordination with the metal atom occurs simultaneously (a) with or (b) before electrophilic attack at the C atom.



There is no kinetic difference between these two mechanisms as with both mechanisms the total order is second, being first order in each reagent. It follows from the structure of the transition state of the limiting step that both mechanisms may be classified as  $S_{R2i}$ .

In principle, however, the reaction may occur with nucleophilic attack at the metal atom being the limiting step:

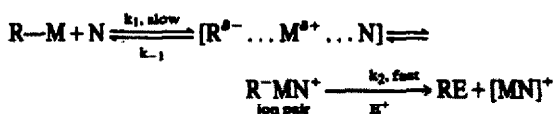
$$k_2 \gg k_{-1} \quad (\text{rate} = k_1 [RM] [EN])$$

where  $k_1$  is the second order reaction rate constant. Examples of such reactions are at present very few, but the propolysis of triethylboron with carboxylic acids, as studied by Dessy *et al.*, may be cited as an example.<sup>72</sup>

Such a mechanism is usually indicated by the effect of substituents on the reaction rate. In the particular example mentioned above, the strongest acids were found to be the least active. The symbol  $S_{R2i}$  has been proposed for this mechanism.<sup>75</sup>

There are very few reactions which may be considered as exhibiting the "pure"  $S_{R2}$  mechanism. Examples are the cleavage of diphenylmercury in acetic acid with perchloric acid and the reaction of  $Alk_2Hg$  with mercury nitrate. However, again in such cases, nucleophilic coordination (although weak) with the metal atom cannot be entirely ruled out.

$S_{R1}$  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  $S_{R2}$  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  $S_{R1}(N)$  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:



(rate =  $k_1 [RM] [N]$ , if  $k_2 \gg k_{-1}$ ; N = nucleophile, M = metal).

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  $S_{R1}$  and  $S_{R2}(S_{R2i})$  mechanism is very difficult, since a kinetic order of 2 would apply in both cases.

The first evidence for  $S_{R1}$  mechanism came from the study of mercuryisotope exchange of ethyl  $\alpha$ -bromo-mercuryphenylacetate with  $^{203}HgBr_2$  in DMSO.<sup>9,76</sup>



The reaction is of first order in the organomercury compound and zero order in mercury bromide. The first

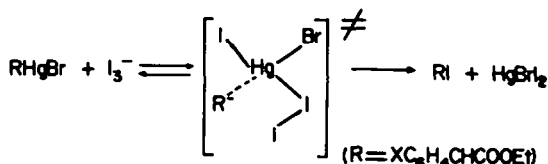
step involves ionization of the organomercury compound, such ionization being facilitated by aprotic dipolar solvents such as DMSO; in the second step the ion pair so generated reacts rapidly with an electrophile ( $\text{HgBr}_2$ ). The degree of ionization in the transition state is apparently influenced by the strength of the nucleophile and the stability of the carbanion in the ion pair. The relatively stable anion of phenylacetic ester ( $\text{pK}_a \sim 17$ ) becomes planar, and as a result racemization occurs.<sup>24</sup>

Studies of the symmetrization reaction of substituted ethyl  $\alpha$ -bromomercuriphenylacetates with ammonia in chloroform showed that the reaction was second order in the organomercury compound and also second order in ammonia,<sup>25</sup> however the observed effect

coordination properties of mercury. The retention of stereochemical configuration in this  $\text{S}_{\text{E}}1(\text{N})$  type reaction arises from the necessary orientation of the reagents associated with the  $\text{Br} \rightarrow \text{Hg}$  coordination.

The observed formal second order kinetics and "abnormal" (in terms of  $\text{S}_{\text{E}}2$  mechanism) substituent effects in reactions of ethyl  $\alpha$ -bromomercuriphenylacetate with  $\text{I}_3^-$ ,  $\rho = 2.3$  may be explained in a similar fashion.<sup>77</sup>

The  $\text{I}_3^-$  anion behaves not only as an iodinating agent in the reaction, but also as a nucleophilic catalyst [ $\text{S}_{\text{E}}1(\text{I}_3^-)$  mechanism]. It is suggested that the complex,  $\text{RHgX} \cdot \text{I}_3^-$ , is formed initially in this reaction, and that further slow ionization occurs along the C-Hg bond; such a pre-equilibrium step is always involved when the solvent functions as a nucleophile.



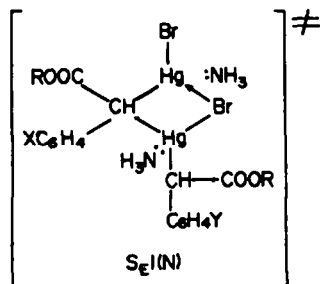
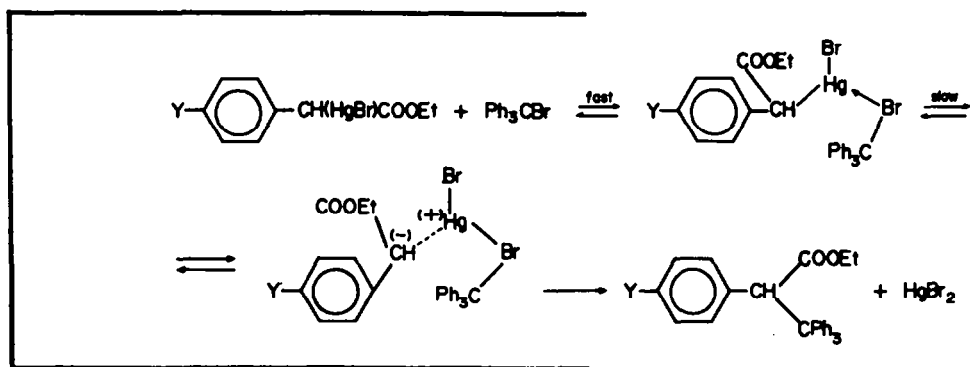
Probably the best illustrative example of such reactions is the reaction of ethyl  $\alpha$ -bromomercuriphenylacetate with triphenylbromomethane. This reaction, which, depending on the nature of the solvent gives either C- or O-tritylation products,<sup>78</sup> involves as a fast step the formation of the complex  $\text{RHgX} \cdot \text{Ph}_3\text{CBr}$ . This complex undergoes decomposition by a first order process, and the effect of substituents Y in the phenyl group ( $\text{NO}_2 > \text{Hal} > \text{H} > \text{alkyl}$ ) is in accord with the assumption that the C-Hg bond ionization is the rate limiting step.<sup>79</sup>



of substituents  $\text{NO}_2 > \text{Hal} > \text{H} > \text{alkyl}$  ( $\rho = 2.8$ ) did not agree with the designation of the reaction as  $\text{S}_{\text{E}}2$ .<sup>32</sup>

Earlier this reaction had been assigned to the  $\text{S}_{\text{E}}2$  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  $\text{Br}-\text{Hg}$  (Y is an electron-releasing substituent and the cleavage of C-Hg



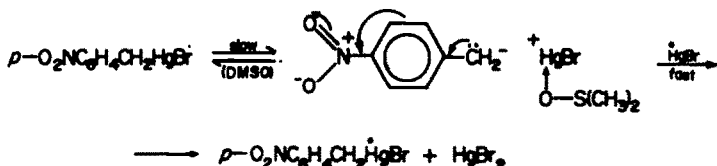
bond (X is an electron-withdrawing substituent).<sup>33</sup> All these facts can now be readily explained on the assumption that the correct reaction mechanism is  $\text{S}_{\text{E}}1(\text{N})$ , with the second reagent molecule bearing a coordinated ammonia molecule behaving as a nucleophilic catalyst (or assistor this behaviour being in line with the known

Thus, triphenylbromomethane acts not only as an electrophilic agent but also as a nucleophilic catalyst, and the reaction may be assigned an  $\text{S}_{\text{E}}1(\text{Ph}_3\text{CBr})$  mechanism.

It is noteworthy that when this reaction is carried out with the complex  $\text{Ph}_3\text{CBr} \cdot \text{HgBr}_2$ , second order kinetics are observed and the substituent effects agree with the  $\text{S}_{\text{E}}2$  mechanism, i.e.  $\text{alkyl} > \text{H} > \text{Hal} > \text{NO}_2$  (negative  $\rho$ ). It is evident that even with the complex  $\text{Ph}_3\text{CBr} \cdot \text{HgBr}_2$ , some  $\text{Br} \rightarrow \text{Hg}$  coordination takes place (i.e.  $\text{S}_{\text{E}}2$  mechanism), since the stronger electrophilic agent,  $\text{Ph}_3\text{CClO}_4$ , 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  $S_{\text{N}}1$  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"  $S_{\text{N}}1$  and  $S_{\text{N}}2$  mechanisms and which, indeed, are of more common 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  $^{203}\text{HgBr}_2$  in quinoline and DMSO has been found to occur by the  $S_{\text{N}}2$  mechanism.<sup>60,61</sup> The only exception is *p*-nitrobenzylmercury bromide, which reacts by the  $S_{\text{N}}1(\text{N})$  mechanism in DMSO.<sup>61</sup>



Thus, introducing a *p*-nitro group (or  $\alpha$ -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<sup>62</sup> in the reactions of a series of substituted benzylmercury chloride with  $\text{I}_3^-$ , which are second order. Substituent effects on the reaction rate are of the usual pattern for the  $S_{\text{N}}2$  (or  $S_{\text{N}}1$ ) 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,  $\text{R}_2\text{Hg}$ , by  $\text{HCl}$  in DMF as a solvent.<sup>63</sup> The plot of Fig. 2 shows the dependence of the protolysis rate constants on the  $\text{p}K_{\text{a}}$  values of the corresponding carbon acids  $\text{RH}$ .

It is clear that the plot has two branches: in the case of stable carbanions the  $\text{R}_2\text{Hg}$  protolysis rate decreases with decreasing acidity of  $\text{RH}$ , whereas for unstable carbanions the rate increases with  $\text{p}K_{\text{a}}$ . These results can be explained if in the particular series of organomercury compounds investigated the  $S_{\text{N}}1(\text{N})$  mechanism is assumed to change to  $S_{\text{N}}2$ .

The  $S_{\text{N}}1$  mechanism has been proposed for several other reactions.<sup>64-67</sup>

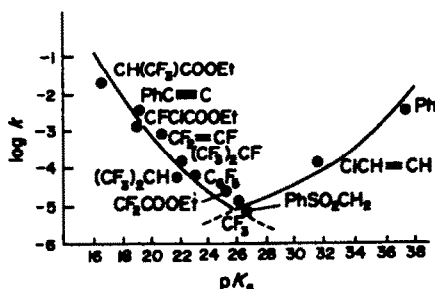
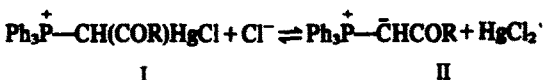


Fig. 2. Dependence of the protolysis rate constants on the  $\text{p}K_{\text{a}}$  values of the corresponding carbon acids,  $\text{RH}$ .

The following equilibrium in  $\text{DMSO}^{68}$  may be formally regarded as involving  $S_{\text{N}}1$  reactions:



In this case the ease of ionization of the C-Hg bond is associated with formation of the stable carbanionic center in the phosphorus ylide, II. The reactivity of compound I has been discussed in Refs. (89-91).

### 8.1 The significance of $\text{p}K_{\text{a}}$ values in organometallic chemistry

$\sigma$ -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,  $\text{R}_2\text{Hg}$ .<sup>92-94</sup> For the estimation of CH-acidities the redox properties of organomercury compounds are used since the  $\text{R}_2\text{Hg}$  reduction potentials are very sensitive to changes in the organic group structure. The relation between  $\text{p}K_{\text{a}}$  values of CH-acids,  $\text{RH}$ , and electrochemical properties of the respective organomercury compounds,  $\text{R}_2\text{Hg}$ , is given by eqn (1):

$$\Delta(\alpha n_{\text{e}} E_{1/2}) = \rho \times \Delta \text{p}K_{\text{a}} \quad (1)$$

where  $\Delta \text{p}K_{\text{a}}$  is the difference between  $\text{p}K_{\text{a}}$ 's for a pair of CH-acids,  $E_{1/2}$  the half-wave potential for  $\text{R}_2\text{Hg}$ ,  $\alpha$  the electrochemical transfer coefficient (which is, in a sense, analogous to the Brønsted coefficient) and  $n_{\text{e}}$  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.<sup>95,96</sup>

This scale covers a more complex scale of  $\text{p}K_{\text{a}}$ 's than any other in the literature: it involves CH-acids with  $\text{p}K_{\text{a}}$ 's from 0 to 60, such as alkanes, arenes, alkenes,<sup>94</sup> haloforms,<sup>97</sup> carboranes,<sup>98,99</sup> heterocyclic aromatics,<sup>100</sup> etc. It has been shown that eqn (1) applies not only to organomercury compounds but also to cobalt (III) and palladium (II) complexes.<sup>101</sup> The only parameter in eqn (1) which is not accessible by theoretical calculation is the  $\rho$  constant. This constant must be estimated experimentally from some representative points.

$\text{p}K_{\text{a}}$  values provide a quantitative measure of carbanion stabilities.

The thermodynamic stability of carbanions in organometallic compounds  $\text{R-M}$  may be defined by the equilibrium constant  $K_{\text{M}}$  of the reaction:



where

$$K_{\text{M}} = \frac{(\text{R}^-)(\text{MN}^+)}{(\text{R-M})(\text{N})}$$



The greater is the value of  $K_M$  the more stabilized will be the carbanion  $R^-$ . The equilibrium constant  $K_M$  is also a measure of the affinity of the carbanion to the metal cation  $M$ . In the majority of cases values of  $K_M$  are unknown (except for very stable carbanions of the type  $CN^-$ ). Thus the relative stability of the carbanion is generally judged from the acid dissociation constant ( $K_a$ ) of the corresponding hydrocarbon  $RH$ .<sup>94</sup>



In a previous study<sup>94</sup> it was shown that there is a linear dependence between the proton affinities ( $pK_a$ ) and mercury cation affinities ( $pK_M$ ) of some O- and N-bases, and these ideas were extended to similar dependences for CH-acids:

$$\log K_M = A \log K_a + B, \quad \text{or} \quad \log K_M = -\Delta pK_a + B. \quad (2)$$

Assuming that such dependence also applies with other elements, i.e. that carbanion affinities towards both the metal cation and the proton are related in a similar fashion, one may use the  $pK_a$  value to characterize the carbanion thermodynamic stability in solutions. The  $pK_a$ 's of some CH-acids and the MSAD scale are listed in Table 5.

Table 5. Expanded MSAD scale of acidities of CH-acids  $RH$ <sup>102</sup>

R in RH	$pK_a$	R in RH	$pK_a$
cyclo- $C_6H_{11}$	45	$(CF_3)_2CH$	22
$(CH_3)_2CH$	44	$CH_2COOC_2H_5$	21
$C_2H_5$	42	m-carboranyl	21
$CH_3$	40	$CF_2=CF$	20
cyclo- $C_3H_5$	39	$C_6H_5C=O$	18.5
$C_6H_5$	37	$CFCOOC_2H_5$	18
$CH_2=CH$	36.5	o-carboranyl	18
$C_6H_5CH_2$	35	$CH(CF_3)COOC_2H_5$	16
p-carboranyl	33	cyclo- $C_3H_5$	15.5
$C_6H_5SO_2CH_2$	27	$CCl_3$	15
$CF_3$	26.5	$CF(CF_3)COOC_2H_5$	14
$CF_2COOC_2H_5$	25	$C(CF_3)_2COOC_2H_5$	14
$CH_2COOCH_3$	24.5	CN	12
$C_6F_5$	23	$CBR_3$	9
$(CF_3)_2CF$	22.5	$(CF_3)_2C$	7

The MSAD scale does not take into account solvent effects upon the hydrocarbon acidities, but in a semi-quantitative comparison these effects may be ignored.

For a detailed analysis of the influence of structure upon hydrocarbon acidity the reader is referred to Cram's monograph<sup>103</sup> and reviews.<sup>96,104</sup>

The use of  $pK_a$  values for elucidating the relation between structure and reactivity of organometallic compounds in  $S_{E1}$  reactions is based on the Brønsted principle:

$$\log k_1 = \alpha \log K_M + C \quad (3)$$

where  $k_1$  is the dissociation rate constant of the organometallic compound in the presence of a nucleophile  $N$ ,  $\alpha$  is the Brønsted exponent (usually  $0 < \alpha < 1$ ),

<sup>†</sup>Nonlinearity of the  $\log k - pK_a$  plot may also be due to a change of  $\alpha$  (eqn 2), as occurs when there is a sufficiently wide change of the  $\log K_M$  range for a particular range of organometallic compounds  $R-M$ .<sup>105</sup>

and  $C$  is a constant. From eqns (2) and (3) it follows that:

$$\log k_1 = -\alpha \Delta pK_a + \text{constant}, \quad (4)$$

i.e. a linear dependence should exist between the logarithms of the dissociation rate constants of the organometallic compounds,  $R-M$ , and the acidities of the corresponding CH-acids,  $RH$ .

It should be noted, however, that the  $S_{E1}$  mechanism is not dissociative but ionizative in nature. Hence the configuration of the cryptocarbanion in the ion pair may be different from that of the free carbanion in solution. For example, in the presence of  $\alpha$ -substituents capable of conjugation ( $NO_2$ ,  $COR$ ,  $CN$ , etc.) the free carbanion has a planar structure; with the ion pair, however, because of cation effect the carbanion configuration may be intermediate between an  $sp^2$  and an initial  $sp^3$  hybridization in the organometallic compound. In such cases the polar effects of  $\alpha$ -substituents in the free carbanion and in the ion pair may vary, (see for example the Hine data<sup>105</sup> for  $\alpha$ -F and  $\alpha$ - $OCH_3$  substituents), and the dependence between the logarithms of the rate constants for  $S_{E1}$  reactions and  $pK_a$ 's (eqn 4) may be nonlinear or nonexistent.<sup>†</sup>

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<sup>107</sup> ( $\log k_1 = 0.17 pK_a + \text{const.}$ ). The linear interrelation between  $\log k_1$  and  $pK_a$  is one of the criteria for assignment of the reaction to  $S_{E1}$ -type.<sup>108</sup>

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.<sup>109</sup> 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 may be written as:

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

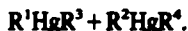
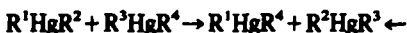


where  $K(R_iHg, R_j)$  is the affinity of carbanion  $R_i^-$  for cation  $R_jHg^+$ . If the affinities of carbanions for organomercury cations and for a proton are linearly dependent,<sup>110</sup> one can write for the reaction of eqn (5) the following expression:

$$\log K_p = (A^1 - A^3) \times \Delta pK_a(R^4H, R^2H) \quad (6)$$

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 6 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 5 is that in which both the Hg 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 5 will be shifted in such a way that the Hg 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.

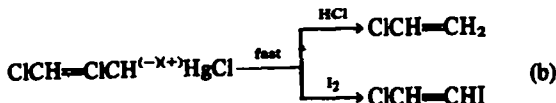


The  $A$  values in eqn (6) characterize the hardness (or softness) of organomercury cations relative to protons. As a rule, a harder cation,  $R_iHg^+$ , corresponds to a stronger acid,  $R_iH$ .

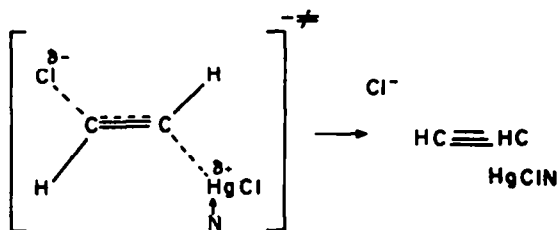
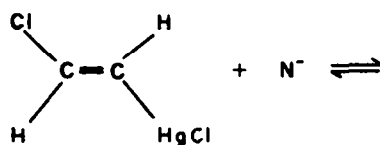
An analogous approach may be used to explain redistribution equilibria in other systems, e.g. in organometallic compounds of Group IVB of the Mendeleev Periodic system (see Ref. 110a).

### 8.2 $S_E1(N)$ reactions at $sp^2$ -carbon atoms

It has been found that both proto- and iodo-demercurations of *trans*- $\beta$ -chlorovinylmercury chloride have an  $S_E2$  mechanism in dioxane, but the mechanism changes in DMSO to  $S_E1(N)$ .<sup>42,111,112</sup>



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.<sup>113</sup> 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  $\beta$ -position, and this leads to acetylene formation.



It is interesting to note that not only  $S_E2$  but also  $S_E1(N)$  reactions of  $\beta$ -chlorovinylmercury chlorides proceed with retention of geometrical configuration, for instance, see Scheme 3, below.

The isotopic exchange of phenylmercury bromide with  $^{203}HgBr_2$  has an  $S_E2$  mechanism in benzene, methanol, DMF, DMSO and other solvents.<sup>114</sup>

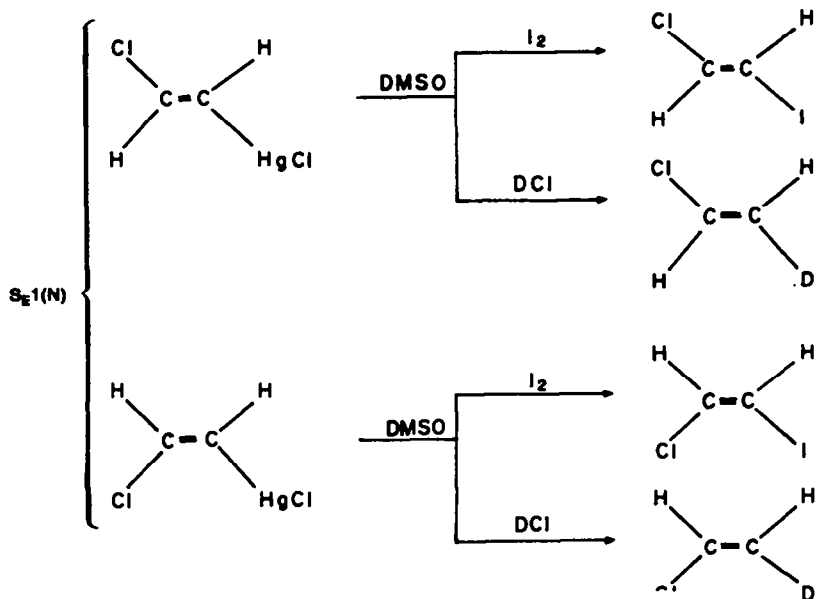
Pentafluorophenylmercury bromide reacts with  $^{203}HgBr_2$  in DMSO by the  $S_E1(N)$  mechanism.<sup>115</sup>



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

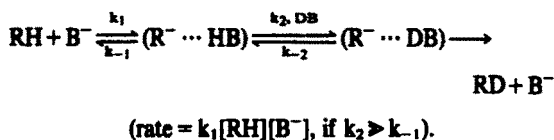
### 8.3 $S_E1(N)$ reactions in purely carbonic systems

It is easy to understand that hydrogen isotopic exchange reactions of hydrocarbons catalyzed by bases should not be used as models for investigating the regularities of electrophilic substitution reactions (bimolecular electrophilic substitution), since the limiting step in such reactions proceeds through nucleophilic attack of base at the hydrogen atom, while interactions with the electrophile occurs in a subsequent fast step. Such a mechanism is supported by a large isotopic effect,

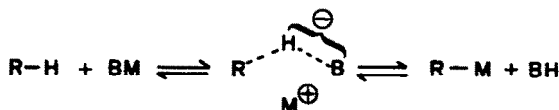


Scheme 3.

the specificity of the exchange reactions making it possible to employ the Brønsted principle [ $\log k = f(\log K_{eq})$ ] to these systems, and thus allowing the use of hydrogen isotopic exchange for determining hydrocarbon kinetic acidities.<sup>116</sup>



A similar mechanism has been proposed<sup>117</sup> for metalation of hydrocarbons:

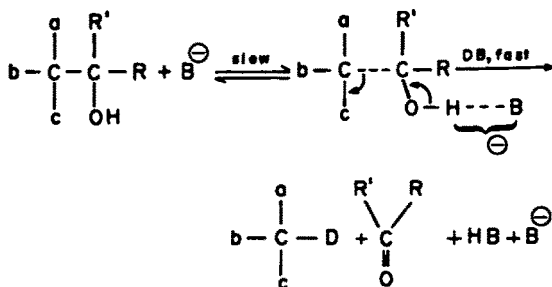


This type of mechanism has been described as "protophilic",<sup>117</sup> and it may readily be seen that it is identical with the  $S_{E1}(N)$  mechanism which has been discussed above for the organometallic compounds.

Numerous studies of the stereochemistry of isotopic exchange, carried out by Cram *et al.*,<sup>103</sup> involving various systems have established that varying the conditions of a reaction (type of base and solvent) may substantially alter the latter stereochemically. Thus the hydrogen isotopic exchange reaction of 2-phenyl-2D-butane in *t*-BuOH-*t*-BuOK as a solvent proceeds with retention of reactant configuration (80-90%), while in DMSO-*t*-BuOK (involving negligible quantities of *t*-BuOH) complete racemization occurs. Diethyleneglycol as solvent causes partial inversion of the configuration.

These effects were attributed to the formation of various intermediates i.e. ion pairs and free ions which do not behave in a similar fashion during solvation by the solvent.

Cram *et al.*<sup>103</sup> also undertook a detailed study of the stereochemistry of electrophilic reaction at the carbanion center (the carbanion resulting from C-C bond cleavage by the base) in the system:

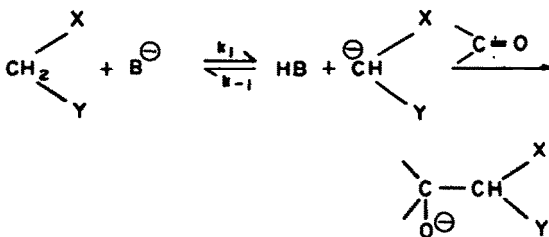


(for example  $a = Ph$ ,  $b = Me$ ,  $c = Et$ ).

As in the case of isotopic exchange, the stereochemistry is found to vary from almost entire retention of configuration in some cases to its substantial inversion in other cases. It can be easily seen that the reaction mechanism has much in common with the mechanism proposed for hydrogen isotopic exchange reactions and may be classified as of the  $S_{E1}(N)$  type.

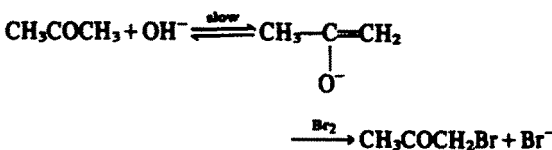
A number of reactions occur in the organic chemistry in which formation of carbanions or cryptocarbanions at a stationary concentration may be assumed as the limit-

ing step.<sup>118</sup> Thus, the variety of carbonyl-methylene condensations which occur during carbanion center formation (as a result of a proton cleavage from the methylene component) in the reaction with base may involve such a mechanism:



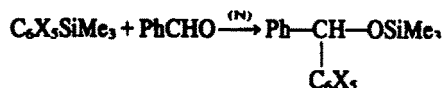
Since, with such a mechanism the rate =  $k_1[CH_2XY][B]$ , these reactions should also be assigned as  $S_{E1}(N)$  type reactions.

The classical reaction involving the bromination of acetone in the presence of base may be cited as another example<sup>119</sup>



together with similar reactions with bromide ion participation which are known to possess virtually identical rates of bromination and of hydrogen isotopic exchange in reactions catalyzed by bases.<sup>103</sup>

Finally a few words should be said about practical conclusions which follow from the above discussion of  $S_{E1}(N)$  reactions of organometallic compounds. It has been mentioned that organometallic compounds with organic groups having strong electron-attractive properties are less reactive in electrophilic bimolecular substitution reactions ( $S_{E2}$  and  $S_{E1}$ ). Such compounds may cleave, however, even with water, if the reaction mixture contains a suitable nucleophilic catalyst ( $S_{E1}(N)$  mechanism). Thus by the use of nucleophilic catalysts it may be possible to effect reactions of these compounds as potential carbanion donors which can be employed on a larger scale in practical organic synthesis. As an example the recently discovered "Grignard" reaction of pentahalophenyltrimethylsilane with benzaldehyde<sup>120</sup> may be cited.



( $X = F$  or  $Cl$ ).

Another interesting example of the application of  $S_{E1}(N)$  reactions in organic syntheses is the use of trihalomethyl organometallic compounds for the preparation of dihalocarbenes under relatively mild conditions.<sup>121-124</sup>

From relative rates of R-M bond cleavage in a series involving one type of metal derivative it is possible to attempt an estimate of the order of reactivity of various organic groups R, i.e. to arrange such groups in order of their changing nucleophilicity.  $S_{E1}$  reactions cannot serve as a relative measure of R group nucleophilicity, however, because the reactivity of an organometallic

compound is affected by its ability to coordinate the nucleophilic part of electrophilic agent and its tendency towards solvation. Even qualitative attempts to a construct "reactivity" series for various organic groups R show numerous deviations. Thus for a series of organomercury<sup>125</sup> and organotin<sup>126</sup> compounds it may be shown that effect of a change in R structure on the rates of acidic cleavage do not coincide.

For this reason the reactivity sequence  $\text{CH}_2=\text{CH} > \text{CF}_2=\text{CF} > \text{Et}$  obtained from  $\text{R}_3\text{H}_g$  decomposition in excess  $\text{HCl}$ <sup>127</sup> is probably more a consequence of the fact that the compounds  $(\text{CF}_2=\text{CF})_2\text{Hg}$  and  $\text{CF}_2=\text{CF}-\text{Hg}-\text{C}_2\text{H}_5$  are capable of exhibiting  $\text{S}_{\text{E}}1(\text{N})$  mechanisms under the reaction conditions employed than of any other reason.

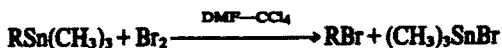
### 9. THE ROLE OF THE ION PAIR IN $\text{S}_{\text{E}}$ REACTIONS

In the study of the reactions of halogen- and mercuri-destannylation<sup>128-131</sup> it was found that in accordance with  $\text{S}_{\text{E}}2$  mechanism the reaction rate goes down in transition from  $\text{C}_6\text{H}_5\text{SnMe}_3$  to  $\text{C}_6\text{F}_5\text{SnMe}_3$ ; in the case of organotin compounds with stronger electron withdrawing groups ( $\text{R} = \text{PhC}\equiv\text{C}$ , fluorenyl, indenyl) the reaction rate sharply increased although the reaction followed the second order:<sup>129-132</sup>



$$k_2^{27} \text{ l mole}^{-1} \text{ sec}^{-1}$$

R = All	$\text{C}_6\text{H}_7$	$\text{PhC}\equiv\text{C}$	$\text{CH}_2=\text{CHPh}$
$2.3 \times 10^7$	$9.6 \times 10^6$	$3.4 \times 10^6$	620420
	$\text{CH}_3$	$\text{C}_6\text{F}_5$	
	52.5	46.7	



$$k_2^{27} \text{ l mole}^{-1} \text{ sec}^{-1}$$

R = $\text{C}_6\text{H}_7$	$9-\text{CH}_2\text{C}_{13}\text{H}_9$	Ph
$1.2 \times 10^8$	$4.1 \times 10^4$	$1.35 \times 10^4$

Halogenation of  $\text{RSnMe}_3$  where  $\text{R} = \text{c}-\text{C}_5\text{H}_5$ ;  $\text{MeCOCH}_2$  and  $\text{CN}$  in  $\text{DMSO}$  was of the first order with zero order by  $\text{Hal}_2$ , i.e.  $\text{S}_{\text{E}}1$  mechanism took place.<sup>132</sup>



R	CN	$\text{CH}_3\text{COCH}_2$	$\text{c}-\text{C}_5\text{H}_5$
$k_1^{20} \text{ sec}^{-1}$	0.33	0.25	4.1†

In many reactions mentioned the rates were so high that the study was possible only by the stopped-flow technique. Similar regularities in the substituent effect were observed in the reactions of organogermanium compounds.<sup>133</sup> Note that all the reactions considered went only with cleavage of  $\text{R}-\text{Sn}(\text{R}-\text{Ge})$  bond. It was assumed that the increased reaction ability of organotin compounds with sufficiently strong electron withdrawing groups is due to the participation of ionic pairs formed in the pre-equilibrium stage rather than to covalent-struc-

tured forms of an organometallic compound, i.e. by ion-pair  $\text{S}_{\text{E}}2$  mechanism ( $\text{S}_{\text{E}}2\text{ip}$ ).



In authors opinion, this mechanism must take place when "nucleophilicity" of R is too low for the direct electrophilic attack by  $\text{S}_{\text{E}}2$  mechanism while carbanion R stability is insufficient for  $\text{S}_{\text{E}}1(\text{N})$  mechanism. In this case the situation may arise when electrophilic attack at ion pair in the rate-determining step will prove to be the most effective.

The mechanism suggested is in the direct analogy with nucleophilic substitution where  $\text{S}_{\text{N}}2$  ion pair mechanism is proposed by Snee as a "unified" nucleophilic substitution mechanism.<sup>134</sup> In the case of nucleophilic substitution this mechanism is most likely to take place for secondary structure while for primary and tertiary derivatives it is supposed to represent the extreme cases, i.e. common  $\text{S}_{\text{N}}2$  and  $\text{S}_{\text{N}}1$  mechanisms. At present, however, the arguments in favour of  $\text{S}_{\text{N}}2$  ion pair mechanism are nearly out-balanced by the arguments against. No direct evidence of the existence of such mechanism has been obtained,<sup>135,136</sup> although this concept does not contradict the theoretical calculations and is generally appealing.<sup>137</sup> The essential feature of Snee's mechanism is the assumption of contact ion pair formation in the pre-equilibrium stage with resulting inversion of configuration at substitution.  $\text{S}_{\text{N}}1$  Mechanism would require the transition of contact ion pair into solvent-separated ion pair or free ions in the rate-determining step. Generally, however, this limitation is unnecessary. The observed kinetic regularities may be accounted for by the simple scheme in dependence on the relation of  $k_2$  and  $k_1$  constants.

$$k_{-1} > k_2[\text{EN}] \quad k_{\text{obs}} = Kk_2[\text{EN}] \quad (\text{S}_{\text{E}}2\text{ip})$$

$$k_{-1} \ll k_2[\text{EN}] \quad k_{\text{obs}} = k_1 \quad (\text{S}_{\text{E}}1)$$

Organometallic chemistry is a rewarding field for such studies and for discernment of various mechanisms since the ionicity of the  $\text{R}-\text{M}$  bond may vary over a wide range due to the change in the nature of carbanion and metal, not to mention the effect of solvent on ionization of organometallic compounds.

Recently it was quite unexpectedly found that the latter factor strongly affected the state of organotin compounds in solution. It was shown that some of  $\sigma$ -bonded organotin compounds containing electron withdrawing groups in sufficiently polar solvents are capable of ionization or even dissociation.<sup>138</sup> UV spectroscopy and conductometry were employed. Electronic spectra of 9-substituted fluorenyl and indenyl derivatives of tin in heptane are close to the spectra of the corresponding hydrocarbons which indicated their covalent form. The spectrum of  $9-\text{CNC}_{13}\text{H}_9\text{SnMe}_3$  in HMPA is, however, identical to the spectrum of the corresponding cesium salt. The position of maximums of adsorption ( $\lambda_{\text{max}}$  458, 432, 407 nm) and the ratio of extinction coefficients are not changed at dilution which points at the formation of free ions or solvent-separated ion points in solutions of organotin compounds as spectral characteristics of these species are practically identical. Conductometric studies showed that free ions were formed since equivalent conductivity remained unchanged over  $(2-8) \cdot 10^{-3} \text{ M}$

†The rate constant for reaction with bromine in 1:1 DMF- $\text{CCl}_4$ .<sup>131</sup>

range of concentrations ( $\lambda = 108 \Omega^{-1} \text{ mole}^{-1} \text{ cm}^2$ ). The complete dissociation of 9-CNC<sub>13</sub>H<sub>9</sub>SnMe<sub>3</sub> in HMPTA is also confirmed by the closeness of rate constant values of alkylation of 9-cyanofluorenyl derivatives of cesium ( $k_2^{20^\circ} = 7.8 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ )<sup>139</sup> and tin ( $k_2^{20^\circ} = 3.1 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ). 9-CNC<sub>13</sub>H<sub>9</sub>SnMe<sub>3</sub> in acetonitrile and pyridine may also dissociate into free ions, although the dissociation is not complete. The degree of dissociation in MeCN is only 1.2% at  $c = 6.8 \times 10^{-3} \text{ M}$ . Dissociation is inhibited by the admixture of Me<sub>3</sub>SnBF<sub>4</sub> which forms common ion Me<sub>3</sub>Sn<sup>+</sup>.

In Table 6 are given the values of dissociation constants for 9-CNC<sub>13</sub>H<sub>9</sub>SnMe<sub>3</sub> in the number of solvents.

Table 6. Values of the dissociation constants for 9-CNC<sub>13</sub>H<sub>9</sub>SnMe<sub>3</sub> in various solvents

	DMF	MeCN	Py	HMPTA
$K^{18^\circ} \text{ mol l}^{-1}$	—†	$(3 \pm 1) \times 10^{-3}$	$(1.2-0.4) \times 10^{-3}$	—‡
$DN_{\text{SnCl}_4}^{140}$	19.2	14.1	33.1	38.8
$20^\circ$	4.3	38	12.3	30

†Conductances of the solution and pure solvent are identical.

‡Completely dissociated at concentrations lower than  $10^{-2} \text{ M}$ .

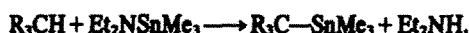
These constants show that dissociation is determined by the donor ability of the solvent characterized by the Gutmann donor number<sup>140</sup> rather than dielectric constant. Besides, the ability of RSnMe<sub>3</sub> to dissociation and ionization is determined by the nature of the R group. Unsubstituted fluorenyl and indenyl derivatives of tin in the studied conditions are not capable of ionization and dissociation. In the general case the ability to dissociate (or ionize) is determined by carbanion R<sup>-</sup> stability.

R	C <sub>13</sub> H <sub>9</sub>	9-MeC <sub>13</sub> H <sub>9</sub> †	C <sub>9</sub> H <sub>7</sub>
In RSnMe <sub>3</sub> pK <sub>a</sub> RH <sup>67</sup>	21.1 do not dissociate	21.8	20.2
R	9-PhC <sub>13</sub> H <sub>9</sub>	1-Me-3-PhC <sub>9</sub> H <sub>7</sub>	9-CNC <sub>13</sub> H <sub>9</sub>
in RSnMe <sub>3</sub> pK <sub>a</sub> RH <sup>67</sup>	18.6 complete dissociation	16	11.4

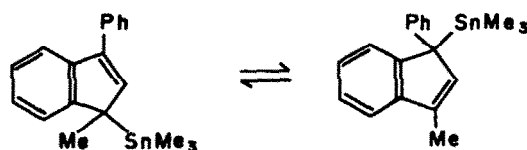
Some compounds, however, dissociate stronger than might be expected from pK<sub>a</sub> values. Thus; 9-phenylfluorenyltrimethyltin dissociates completely although indene and 9-phenylfluorene pK<sub>a</sub> in MSAD scale<sup>103</sup> are identical which is likely to be connected with the influence of steric factors and reduction of steric tension in dissociation.

The results demonstrating the ability of organotin compounds under study to ionization and dissociation is a strong argument in favor of ion pair mechanism in cases when ions and ion pairs are not detected in measurable amounts. The direct proof of ion pair formation in solutions of organotin compounds when their concentrations were stationary was obtained in stereochemical studies. The optically active S-(+)-(3-methylindenyl)-trimethyltin ( $[\alpha]_D^{232^\circ} + 232^\circ$ , C<sub>6</sub>H<sub>6</sub>,  $c = 2.4$ ) and (+) - (1-methyl-3-phenylindenyl)trimethyltin ( $[\alpha]_D^{232^\circ} + 232^\circ$ , C<sub>6</sub>H<sub>6</sub>,  $c = 4.4$ ) were synthesised. The

synthesis was carried out by stannylation reaction of optically active hydrocarbons under the action of diethylaminotrimethyltin on S - (+) - 1 - methylindene ( $[\alpha]_D^{189^\circ} + 189^\circ$ , C<sub>6</sub>H<sub>6</sub>,  $c = 1, 2$ ) and R - (-) - 1 - methyl - 3 - phenylindene ( $[\alpha]_D^{55^\circ} - 55^\circ$ , C<sub>6</sub>H<sub>6</sub>,  $c = 2.2$ ) in benzene.<sup>141, 142</sup>



The study of temperature dependence of <sup>13</sup>C NMR spectra showed that along with (1-methyl-3-phenylindenyl)trimethyltin another isomer, (1-phenyl-3-methylindenyl)trimethyltin was present in equilibrium mixture at room temperature. Fast metalotropic transformation between these isomers takes place.

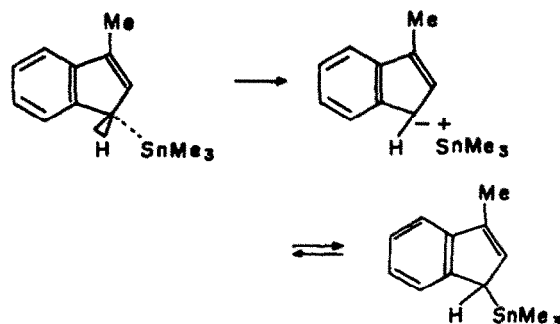


Metalotropic equilibrium is left-displaced and the part of (1-phenyl-3-methylindenyl)trimethyltin is 10-15%.<sup>142</sup> The retention of optical activity shows the intramolecular character of migration.

Optically active indenyl derivatives of tin in low-polar aprotic solvents (C<sub>6</sub>H<sub>6</sub>, dimethoxyethane) are sufficiently stable stereochemically. They then are, however, quickly racemized in pure form or in HMPTA solution (Table 7).

The racemization rate of the two studied organotin compounds is in agreement with their ability to ionize. Thus, (1-methyl-3-phenylindenyl)trimethyltin which is more liable to ionize exhibits a markedly decreased optical activity even in benzene ( $k_1^{20^\circ} = 3.2 \times 10^{-5} \text{ sec}^{-1}$ ,  $c = 0.2 \text{ M}$ ); racemization in CH<sub>2</sub>Cl<sub>2</sub> is still faster. Racemization of (3-methylindenyl)trimethyltin under these conditions is extremely slow.

Evidently loss of stereochemical configuration occurs as the result of ionization (facilitated by the coordination of tin atom with the solvent) with the formation of an ion pair the return of which into the initial stage goes with racemization.



The nature of this ionic pair remains unknown. The return from contact ionic pair in nucleophilic substitution was found to go with retention of configuration. Yet, in the case of carbanionic ion pairs nothing is known about the character of cationic fragment migration around the anionic centre in ion pairs of various types. The formation of solvent-separated ion pairs in the presence of HMPTA seems more probable, their presence in benzene being hardly conceivable.

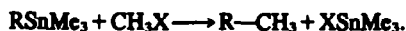
†Ionized (or dissociated) by 2% at  $[R\text{SnMe}_3] = 8.5 \times 10^{-3} \text{ M}$ .

Table 7. Effect of added HMPTA on racemization rate constants for *S* - (+) - (3-methylindenyl)trimethyltin in DME at 16°

[R <sub>3</sub> SnMe <sub>3</sub> ] × 10 <sup>2</sup> M	[HMPTA] × 10 <sup>2</sup> M	τ <sub>1/2</sub> × 10 <sup>-2</sup> min	k <sub>1</sub> × 10 <sup>5</sup> sec <sup>-1</sup>
4.98	0	34.0	0.34†
	1.18	13.8	0.83
	1.88	9.7	1.2
3.72	2.30	6.8	1.7
	4.24	1.9	6.0
	7.77	0.97	12.0
	12.9	0.60	19.3

†In 1:5 DME-THF.

The ability of organotin compounds studied to ionization and S<sub>N</sub>2 ion pair pathway which accounts for their increased reaction ability may be used for synthetic purposes. To demonstrate this aspect of the problem,<sup>143</sup> the reaction of organotin compounds (R-fluorenyl, 3-methylindenyl, indenyl, 9-cyanofluorenyl) in HMPTA and a mixture of tetrahydrofuran - ether (1:1) at 20°. The reaction of alkyldestannylation is known to be non-specific for organotin compounds. It has been shown by glc that in excess of alkylating agent and the sufficient time of the reaction yields of alkyldestannylation products were quantitative.



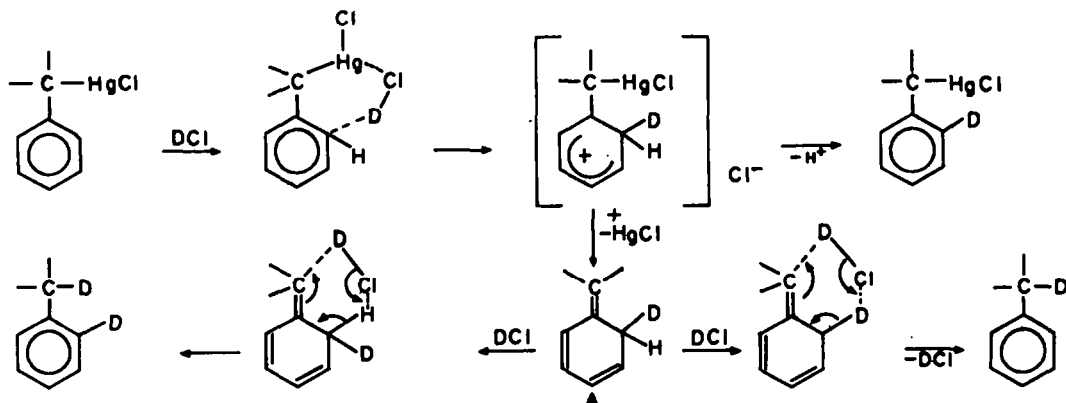
In their reaction ability organotin compounds in this reaction form the series corresponding to the decrease in electron-withdrawing properties of the group.



The reaction ability of methylating agents decreases in the series MeI > MeOTs > Me<sub>2</sub>SO<sub>4</sub>. The effect of the nature of leaving group is characteristic of the reaction of nucleophilic substitution with the participation of "soft" nucleophilic agents.

#### 10. S<sub>2</sub> REACTIONS IN BENZYL ORGANOMETALLIC COMPOUNDS

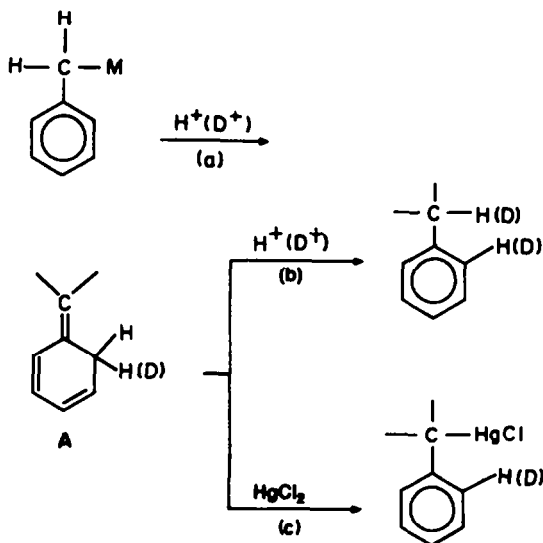
The reaction of BzHgCl with DCl in dioxane gives the following compounds under conditions of pseudomonomolecularity: *o*-DC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>HgCl (I), PhCH<sub>2</sub>D (II), PhCH<sub>2</sub>D (III), *o*-DC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>D (IV). In I and IV, deuterium is found only in *ortho* positions. The following mechanism has been proposed for this reaction.<sup>144</sup>



This mechanism is in agreement with more recent data on deuterio-<sup>145-149</sup> and acetyldemercuration.<sup>150,151</sup>

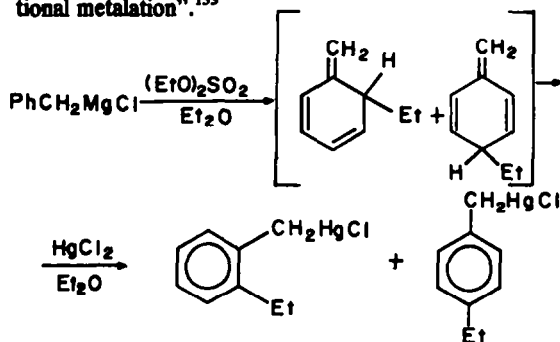
A similar mechanism was proposed for deuteriodemercuration of tribenzyltin chloride.<sup>152</sup>

If the A isomeric form of toluene is indeed formed as an intermediate product during protolysis of benzyl organometallic compounds, its aromatization may well proceed not only under the action of H<sup>+</sup> (D<sup>+</sup>) but also in the presence of other electrophiles, e.g. HgCl<sub>2</sub> (reaction (c)):

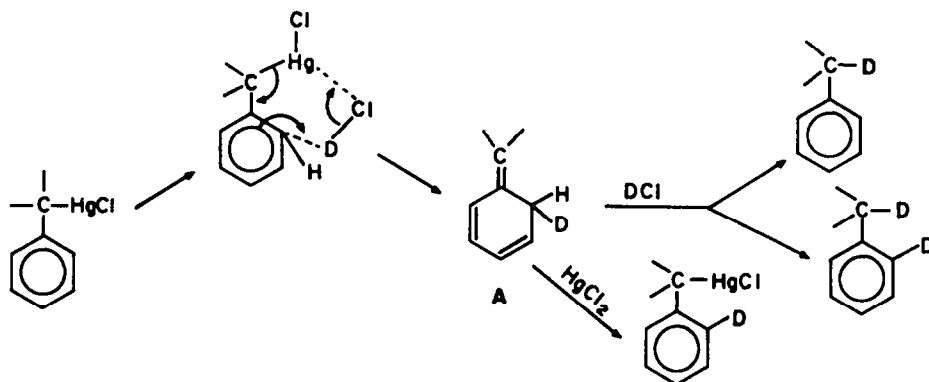


Indeed, addition of HgCl<sub>2</sub> to Bz<sub>3</sub>SnCl + DCl reaction mixture produces Bz-HgCl with deuterium in *ortho* position. Mercuri bromide also acts as a "electrophilic trap" for the arene isomer.

Finally, it was shown that preliminarily prepared methylenecyclohexadienes readily undergo "aromatization metalation".<sup>153</sup>

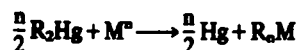


The reaction of aromatization metalation and increase of the rate of  $BzHgCl$  deuterioexchange in *ortho*-position in the presence of  $HgCl_2$  (as well as the absence of deuterated  $BzHgCl$  when the reaction is run to 15-20% of completion) suggests that "conservation" of the metal-carbon bond in the process of isotope enrichment may be only illusory.<sup>154,155</sup> In this case the reaction mechanism may be represented by an elimination-addition scheme:†



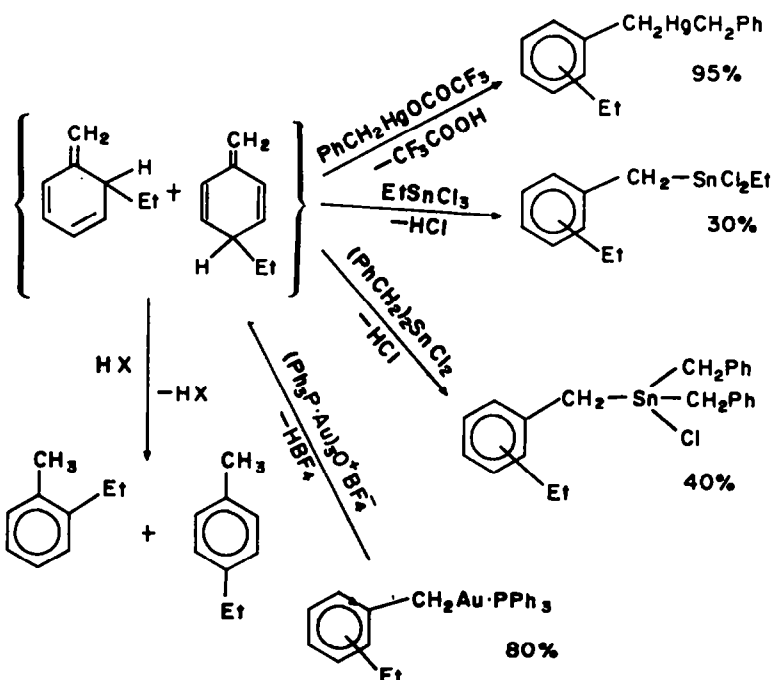
The high reactivity of trienes of the *exo*-methylene-cyclohexadiene type is revealed particularly in relation to reagents for which metalation reactions were not considered typical. In the course of our investigation we discovered the first instances of electrophilic addition of unsymmetrical organometallic compounds,<sup>155</sup> diorganodichloro- and organotrichlorostannanes, triphenylphosphine complexes of univalent gold<sup>156</sup> and of germanium dichloride to unsaturated systems with formation of metal-carbon  $\sigma$ -bond.

compounds by the reaction:



( $M = Li, Na, Be, Mg, Zn, Cd, Al, Ga, In, Sn, Bi, Te$ ) is extensively used and frequently is the main method of synthesis while for certain metals it is the only one.

The study of the mechanism of these reactions was for a long time neglected.

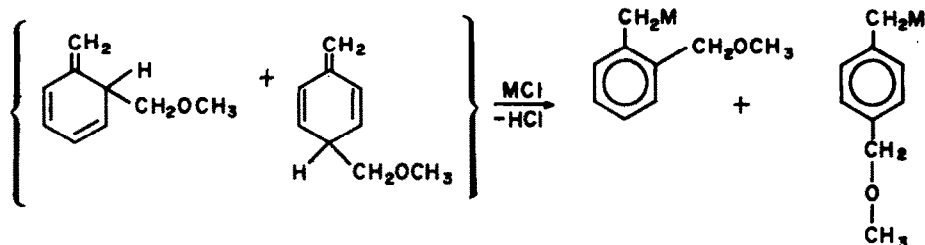


These reactions confirm the general nature of the discovered reaction as a new method of synthesis of benzyl organometallic compounds.

We have examined two of the most simple model reactions of this type:<sup>160-162</sup>

†The reaction mechanism is also discussed in papers.<sup>156,157</sup>



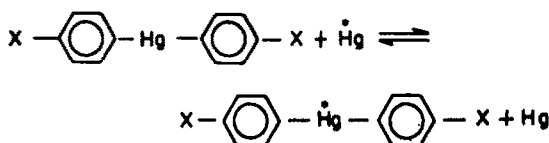


and



Aromatic, beta-chlorovinyl organomercurials and alpha-oxomercuric compounds readily enter into such isotopic reactions (substitution at aromatic, olefinic or saturated carbon in the case of the latter compounds). Reactions proceed in organic solvents in such mild conditions that intermediate formation of free organic radicals is excluded.

The reaction rate for aromatic compounds



is considerably affected by the nature of X, increasing in the sequence

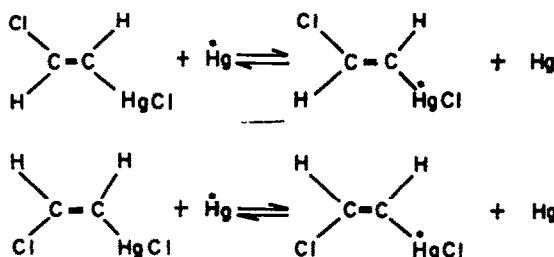


Disproportionation does not occur in the reactions of unsymmetrical compounds with radioactive mercury:<sup>160</sup>

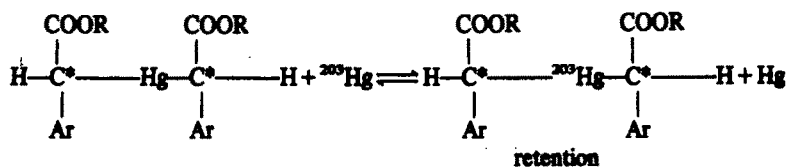


( $\text{Ar}_2\overset{*}{\text{Hg}}$  and  $\text{Ar}'_2\overset{*}{\text{Hg}}$  are not formed).

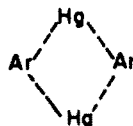
Beta-chlorovinyl compounds react with retention of geometrical configuration<sup>163</sup>



Similar reactions at a saturated C atom proceed with complete retention of the stereochemical configuration, for instance:<sup>5,161</sup>



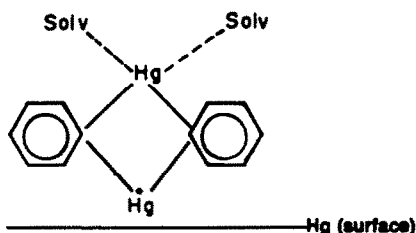
On the basis of the above-mentioned experimental data a cyclic transition state was proposed.<sup>99</sup>



Subsequently, Pollard and Westwood<sup>164,165</sup> carried out a detailed kinetic study of this heterogeneous reaction. They confirmed the data mentioned above in the example of *p*-tolylphenylmercury.

It was shown by means of paper chromatography that only the initial compound is present after exchange, no traces of diphenyl- and ditolylmercury were detected. By carrying out the reactions in controlled conditions the authors were able to achieve an approximately constant degree of fractionation of metallic mercury (constancy of surface) and high reproducibility of kinetic data. The thermodynamic parameters of activation were determined for isotope exchange of 10  $\text{R}_2\text{Hg}$ -type compounds with metallic mercury in benzene. The reaction rate is in good agreement with the Hammett constant of the substituent. For all compounds studied (including dibenzylmercury) an isokinetic relationship is observed (isokinetic temperature  $-384^\circ\text{K}$ ). This can be considered as an indication of a common mechanism. The effect of the substituent at the aromatic ring is typical of  $\text{S}_2\text{N}_2$  reactions.

Taking into account changes of hybridization due to substrate solvation and the fact that the reaction is interfacial it was proposed to depict the transition state as:



The next stage in the study of the reactions under consideration is connected with the application of electrochemical methods. Using the pulse electrochemical technique it was established that contact of  $\text{R}_2\text{Hg}$  with

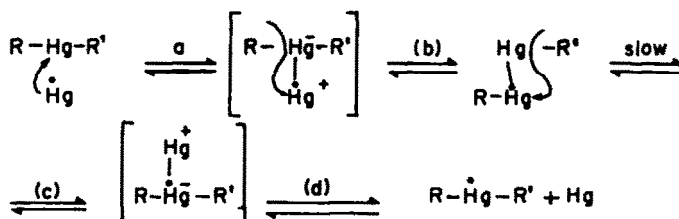


the surface of metallic mercury leads to formation of "organic calomels".<sup>166</sup>



"Organic calomels" are highly unstable† and their life-time varies in the range of  $10^{-2}$  -  $10^{-4}$  sec depending on R.<sup>168</sup>

They apparently are intermediates in the reactions of isotope exchange; the mechanism being represented by the following scheme:

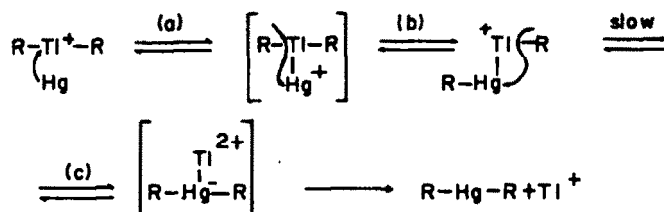


Using the galvanostatic method it was shown that the reaction of *trans*-metalation



proceeds via formation of intermetallic cation,  $RTi^+HgR$ <sup>169</sup> which is an isoelectronic organic calomel.<sup>170</sup>

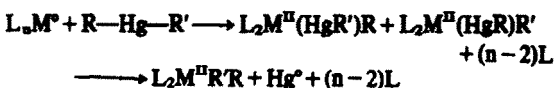
The reaction is presumably similar to the above-mentioned isotope exchange:



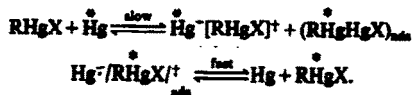
For surveys of studies devoted to these exchange reactions see Refs. 171, 172.

It may be assumed from the above-described investigation of exchange reaction mechanisms that  $R_nMHgR$ -type intermediates are usually formed in reactions of *trans*-metalation involving metallic mercury or organomercuric compounds.

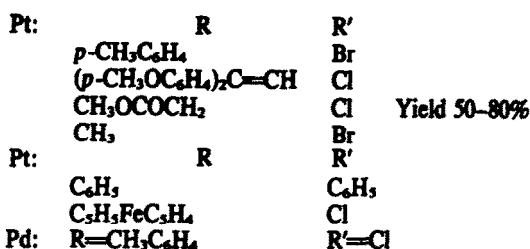
Proceeding from this assumption a new synthesis of  $\sigma$ -Pt and  $\sigma$ -Pd organometallic compounds was developed. The use of this method is apparently limited only by the availability of the appropriate organomercuric compound.<sup>173,174</sup>



†Kreevoy and Walters<sup>167</sup> proposed an oxidation-reduction mechanism assuming intermediate formation of adsorbed organic calomel, for example,

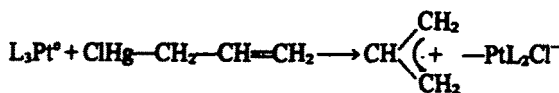


Actually, mercury is a reducing agent and not an oxidizer.<sup>168</sup>



The reactions proceed readily in inert benzene-like

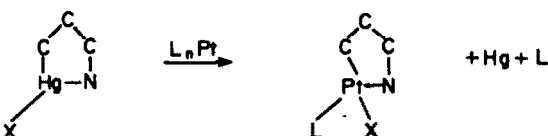
solvents at room temperature (under argon atmosphere). An example of synthesis of an  $\pi$ -allyl complex:<sup>175</sup>



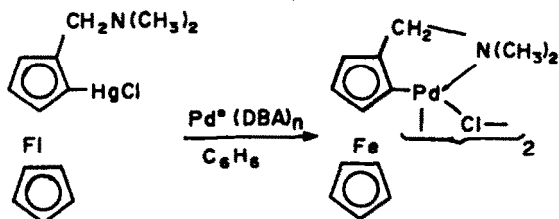
The possibility of intramolecular cyclization consider-

ably stimulates the formation of new carbon-transition metal bonds.

The reaction under consideration turned out to be useful for the synthesis of chelate metallocycles.<sup>176</sup>



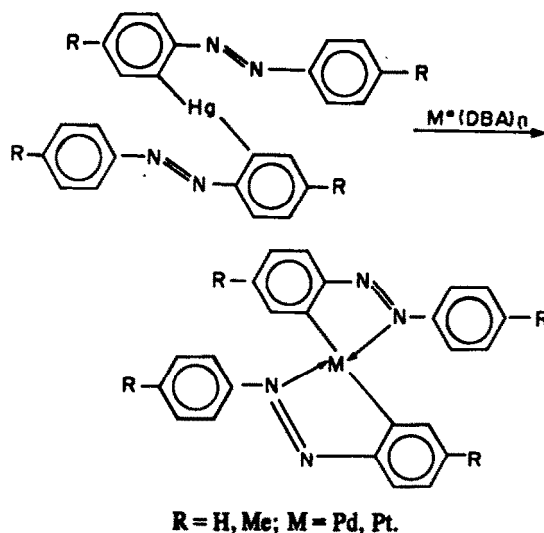
The following example illustrates the synthesis with subsequent enantiomer resolution of 1,2-disubstituted ferrocene with planar chirality.



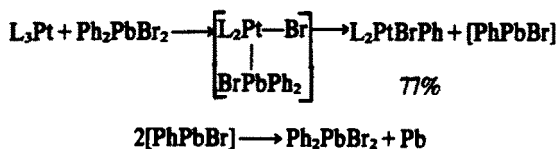
DBA—dibenzylidenacetone Di- $\mu$ -chloro-bis-(2-C,N-dimethylaminomethylferrocenyl)-di-palladium (II).

In the case of a symmetrical organomercuric compound containing chelate-forming groups, a bis-

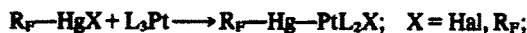
chelate derivative with a "spirane"-type metal atom may be produced as a result of double coordination with elimination of the labile ligand. This reaction was carried out for several azoarenes and rendered with high yields compounds which are difficult to synthesize in any other way.



Zerovalent platinum complexes also react with organolead compounds:<sup>174</sup>



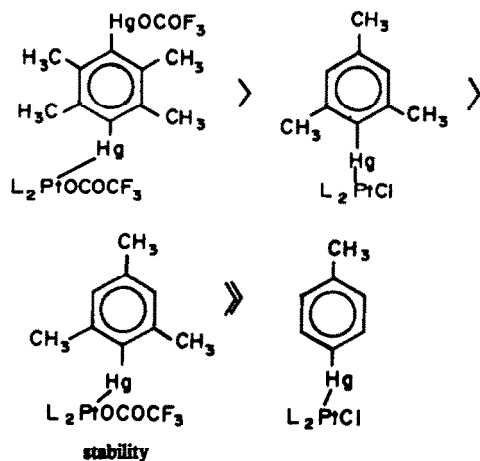
Highly stable compounds with a Pt-Hg  $\sigma$ -bond were synthesized<sup>174,177,178</sup>



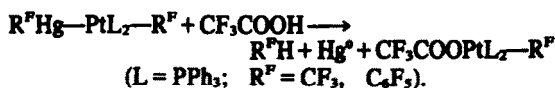
for instance,



The influence of steric hindrance on the stability of the Pt-Hg bond is illustrated by the following sequence:<sup>173</sup>

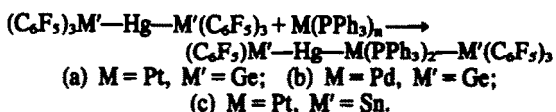


A characteristic reaction of acidolysis was found:<sup>177</sup>



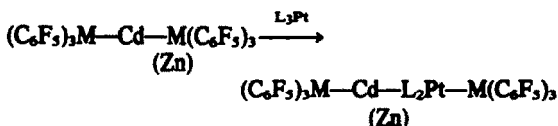
Hence, complex  $L_3Pt$  or the active species  $L_2Pt^0$  corresponding to it, act as a carbenoid, being incorporated at the mercury-element bond. The *cis*-configuration of  $CF_3Hg-PtL_2CF_3$  is consistent with such an interpretation. The  $L_2Pt$  species acts as a nucleophilic carbenoid since the reaction with  $(C_6F_5)_2Hg$  proceeds more rapidly than with  $(C_6H_5)_2Hg$ .<sup>174</sup>

Incorporation of  $(Ph_3P)_2Pt$  and  $(Ph_3P)_2Pd$  along Hg-Ge and Hg-Sn bonds has been realized:<sup>179</sup>



Compounds with oligometallic chains are very stable (they decompose only in boiling trifluoroacetic acid). A stable compound with a Pd-Hg bond was obtained for the first time.

Oligometallic chains containing cadmium or zinc were also synthesized:<sup>179</sup>



Both sigma-bonds were obtained for the first time (Cd-Pt is stable, Zn-Pt is sensitive to oxygen).

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