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# My Way in Organometallic Chemistry\*

A. N. NESMEYANOV

Institute of Organo-Element Compounds  
Academy of Sciences, Moscow, USSR

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## FIRST STEPS

Chemistry has charmed me since 1912 when I was thirteen, my passionate affections for various branches of biology (entomology, hydrobiology, ornithology) being already over. During my summer vacations at my grandmother's, I happened to come across an old shed of my grandfather's where I found the ancient treatise *Inorganic Chemistry* by Richter. This volume was more absorbing to me than the books of my favorite authors

\* Translated by A. V. Grib, Institute of Organo-Element Compounds, Moscow.

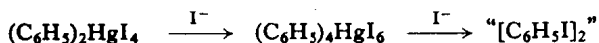
Jules Verne and H. G. Wells. A year later, I set up my own small laboratory and obtained Remsen's *Organic Chemistry*. This, and other books, strengthened my contact with elementary chemistry, so when in 1917 I crossed the threshold of Moscow University for the first time, I was quite familiar with the chemistry of those days. During my first years in the University I was enraptured by the science and nothing but the science of chemistry. As an undergraduate, however, as the challenges of inorganic, physical, and organic chemistry were overcome, I had to make a choice of specialization. I was fond of chemical substances, with their shape, color, and smell, whereas the generalizations of physical chemistry, however useful, seemed to me rather vague. But it was a difficult problem to choose between inorganic and organic chemistry, perhaps, that is why I took the essentially organometallic road. Not wishing to be Buridan's ass and die of hunger between two bundles of hay, I preferred to gather food from both bundles. Formally, however, I declared my adherence to the Organic Chemistry Division. This was caused by the fact that organic and analytical chemistry were headed by Professor N. D. Zelinsky, making this choice more attractive than any of the other possibilities. I was also much impressed by his proposal to work with him as a post-graduate student in 1922. By that time, the extensive scientific interests of Zelinsky were more and more concentrated on catalytic hydrocarbon chemistry, and his co-workers, whose number was constantly increasing, were exploring this field. Of course, this was very attractive and promising, but not for me. Carbon and hydrogen are good, but what about the other 100 elements? Though I was assigned a cyclopropane problem, I did not give it too much attention and looked for something closer to my own interests. Only after many failures, did Fortune in 1927-1928 show me her better face. I had been looking for esters of complex acids such as  $\text{HHg}^{\text{III}}\text{I}_3$  or  $\text{HPb}^{\text{II}}\text{I}_3$ , and a possible isomerism of  $\text{RPb}^{\text{II}}\text{I}_3$  with  $\text{RPb}^{\text{IV}}\text{I}_3$ . To begin with, the esters which had not been described should be synthesized. The direct reaction, e.g.,  $\text{CH}_3\text{I}$  with  $\text{HgI}_2$ , was obviously unsuitable. I attempted to obtain aromatics of the desired type by the decomposition of arene diazonium salts of the complex acids whose esters I was craving for. I prepared a series of such salts, among which were  $(\text{C}_6\text{H}_5\text{N}_2)_4\text{Fe}(\text{CN})_6$  and  $(\text{C}_6\text{H}_5\text{N}_2)_2\text{HgI}_3$ . The decomposition of the former salt with or without Gatterman copper gave two compounds which were hard to separate and purify. One of them was lilac, the other colorless. Each had the composition  $(\text{C}_6\text{H}_5)_2\text{H}_2\text{Fe}(\text{CN})_6$ . I had no time to study them in more detail because simultaneously I had been

examining the decomposition of  $(C_6H_5N_2)HgI_3$  and the results obtained were so interesting that they required my whole attention. So, my lilac and white compounds were never reported.

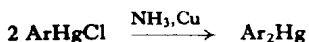
## II

### THE DIAZONIUM METHOD

The salt  $(C_6H_5N_2)HgI_3$  decomposed completely within a few days. The resulting slurry could be purified to give a compound which, interestingly, had the composition  $(C_6H_5)_2HgI_4$  (II), rather than that of the expected "ester"  $C_6H_5HgI_3$  (I). I believed that the former compound was the ester of the acid " $H_2HgI_4$ " and introduced the compound into the reaction most typical of esters, alkaline saponification, viz. saponification by  $I^-$ . You can imagine my bewilderment when my ester reacted according to the scheme



Excess iodide made the mercuric iodide dissolve entirely, leaving a colorless dimeric "iodobenzene" which I had no difficulty in identifying as diphenyliodonium iodide. Thus, all my "esters" were diphenyliodonium salts whose anions were  $HgI_3^-$  or  $HgI_4^{2-}$ . This was a novel route to diphenyliodonium salts, but the disappointment was bitter. In this manner, the first publication containing concepts and experimental results which were my spiritual property appeared (1). However, the copper-initiated decomposition of the initial diazonium salts proceeded in quite another fashion. Instead of the yellow salts (I) and (II), I isolated high-melting plate-like crystals containing Hg, carbon, and iodine. But my glee did not last long. I was already sufficiently familiar with organometallic chemistry to suppose that the compound was nothing but  $C_6H_5HgI$ , which turned out to be precisely the case. One more disappointment. However, the reaction was an absolutely new way to organomercury compounds, so it was worth studying. "Double salts" such as  $C_6H_5N_2^+HgBr_3^-$  or  $C_6H_5N_2^+HgCl_3^-$ , when treated with copper, produced  $C_6H_5HgBr$  or  $C_6H_5HgCl$  in good yields as well. Moreover, I showed that substituted arenediazonium salts, as well as each of the two naphthalenediazonium cations, afforded  $ArHgCl$  compounds, while the "diazo method" as combined with the F. Hein symmetrization,



appeared to represent a one-step synthesis of diaryl mercury compounds. Based on this was my second publication (2), and also the third one (3), in collaboration with E. I. Kan (my first co-worker; she was by that time a student of the University). These have been followed by over 700 papers. The samples of  $C_6H_5N_2HgBr_3$  and  $C_6H_5N_2HgCl_3$  were left in unsealed ampoules. The second salt remained unchanged for years. The first one, in a year, gave a mixture of bromobenzene and a crystalline compound.

TABLE I  
DIAZONIUM ORGANOMETALLIC SYNTHESSES<sup>a</sup>

Metal	Reactions	% yield <sup>b</sup>	Reference
Hg	$ArN_2Cl \cdot HgCl_2 + 2Cu \rightarrow ArHgCl + N_2 + 2CuCl$ $2ArN_2Cl \cdot HgCl_2 + Cu + NH_3 \rightarrow Ar_2Hg + 2N_2$ $+ 2CuCl \cdot am + Hg$	30-80	(2)
Tl	$2ArN_2BF_4 + 2Tl \rightarrow Ar_2TlBF_4 + 2N_2 + TlBF_4$	30-80	(3)*
Sn	$ArN_2BF_4 + SnCl_2 + Zn \rightarrow Ar_2SnCl_2$ $+ (Ar_3SnCl + ArSnCl_3)$	approx 10	(5)
Pb	$4ArN_2BF_4 + PbNa \rightarrow Ar_4Pb + 4N_2 + 4NaBF_4$	10-40	(6, 7)
Sb	$ArN_2Cl \cdot SbCl_3 + Zn \rightarrow ArSbCl_2 + N_2 + ZnCl_2$ $2ArN_2Cl \cdot SbCl_3 + 2Zn \rightarrow Ar_3SbCl_3 + N_2 + 2ZnCl_2$ $+ SbCl_3$	15-30	(8)
	$3ArN_2Cl_3 \cdot SbCl_3 + 3Zn \rightarrow Ar_3Sb + 3N_2 + 3ZnCl_2$ $+ 2SbCl_3$	25-30	(9)
	$3ArN_2Cl \cdot SbCl_3 + 2Zn \rightarrow Ar_3SbCl_2 + 3N_2 + 2ZnCl_2$ $+ 2SbCl_3$	25-30	(9)
	$(ArN_2Cl)_2 \cdot SbCl_3 + 2Zn \rightarrow Ar_2SbCl + 2N_2 + 2ZnCl_2$	25-30	(9)
	$2ArN_2Cl \cdot SbCl_3 + Fe \rightarrow Ar_2SbCl_3 + 2N_2 + FeCl_2$ $+ SbCl_3$	42-46	(10)
	$ArN_2Cl \cdot SbCl_3 + 2CuCl \rightarrow ArSbCl_4 + N_2 + 2CuCl_2$	42-97	(11)
	$ArSbCl_2 + Ar'N_2Cl \cdot SbCl_3 \rightarrow ArAr'SbCl_3 + N_2 + SbCl_3$	10-40	(12)
As	$2ArN_2Cl \cdot FeCl_3 + AsCl_3 + Fe \rightarrow ArAsCl_2 + N_2 + FeCl_3$ $+ FeCl_2$	—	(13, 14)
	$2ArN_2Cl \cdot FeCl_3 + AsCl_3 + 2Fe \rightarrow Ar_2AsCl + 2N_2$ $+ 2FeCl_3 + 2FeCl_2$	20-40	(15, 32)
	$3ArN_2Cl \cdot FeCl_3 + AsCl_3 + 2Fe \rightarrow Ar_3As + 3N_2$ $+ 3FeCl + 3FeCl_2$	20-40	(16, 32)
	$ArAsX_2 + (Ar'N_2Cl)_2ZnCl_2 + 2Fe \rightarrow ArAr'As + 2N_2$ $+ ZnCl_2 + 2FeCl_2$	—	(15, 32)
		30-40	(16, 32)
Bi	$3ArN_2BF_4 + 2Bi \rightarrow Ar_3Bi + 3N_2 + Bi(BF_4)_3$	20-70	(17, 18)

<sup>a</sup> All reactions are carried out in acetone or (in the case of Sb) in ethyl acetate; am is ammonia.

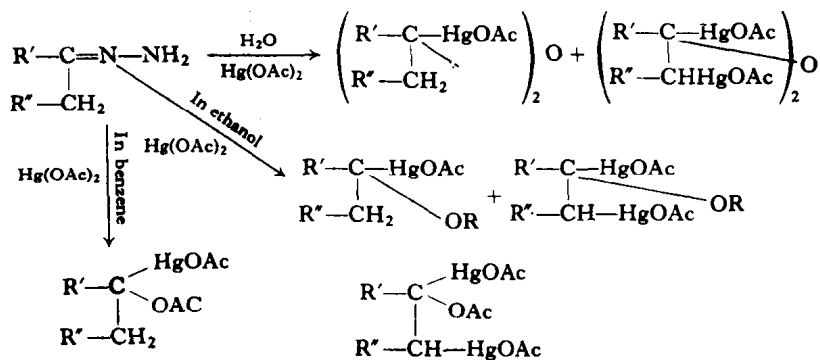
<sup>b</sup> The yield range refers to various aryls, Ar. The yields are the highest with  $C_6H_5$ .

If I had worked up the mixture (as I subsequently did in 1959), diphenylbromonium (and diphenylchloronium) salts could have been reported some thirty years before their actual discovery (4).

But the "diazo method" still had its grip on me. Which metals, apart from mercury, could be subjected to the method? To answer this, many years were to pass because simultaneously I was working on other problems of interest to me. Eventually, the method of synthesis was extensively developed for aromatic derivatives of such elements as Hg, Tl, (Ge), Sn, (Pb), As, Sb, Bi. For the metals in parentheses the method was shown to just work, while for the others it is an excellent preparative procedure. In Table I the best versions are exemplified. At the same time, I and the first generation of my disciples, and also other scientists, applied the method to various organomercurials substituted at the aromatic nucleus (19-21), and to the naphthalene (22), triphenylmethane (23), and pyridine (24) series.

This work was initiated in 1927, and in 1953 the last paper of the series was published. Intermittently, other related investigations were accomplished. Here, I would like to mention the reaction of aliphatic diazo compounds with mercuric chloride. The reaction of methylamine with mercuric chloride under the conditions of the diazo method was unsuccessful. Instead of the methylmercuric chloride expected, the synthesis gave negligible amounts of chloromethylmercury chloride, a compound obtained by Hellerman from mercuric dichloride and diazomethane in good yield. With diazoacetic ester, the compound  $\{\text{ClHg}(\text{Cl})\text{C}-\text{C}(=\text{O})\text{OC}_2\text{H}_5\}_2\text{Hg}$

was obtained (25). Finally, hydrazones of ketones which might form the aliphatic diazo intermediates gave a number of organomercurials in a reaction which, as it was suggested, involved conjugate addition [Nesmeyanov, Reutov, and Loseva (26, 26a)].





The conjugate addition of  $\text{HgOAc}$  and the solvent fragments ( $\text{RO}$  in methanol,  $-\text{O}-$  in water,  $\text{OAc}$  in benzene) was usually accompanied by the mercuriation of the methylene adjacent to the unsaturated carbon atom. In addition, elimination of the second mercury-containing group attached to the  $\beta$ -carbon, together with the solvent fragment attached to the  $\alpha$ -carbon sometimes occurred, giving an  $\alpha,\beta$ -double bond. For example, cyclohexanone produced 1-acetatomercurycyclohexene-1. This  $\beta$ -elimination correlated with the properties of quasi-complex compounds which had been investigated by us extensively.

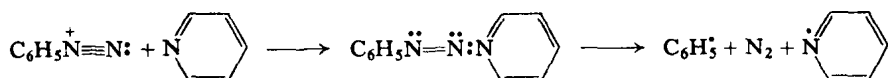
### III

#### **HOMOLYSIS AND HETEROLYSIS OF DIAZONIUM SALTS. SYNTHESIS OF HALOGENONIUM SALTS. THE HALOGENONIUM METHOD**

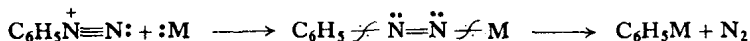
The aliphatic diazonium salts were only a side issue in the research. At the same time, the aromatic tetrafluoroborate salts were studied by me from other points of view. These investigations are outside the framework of organometallic chemistry but they must be described here briefly, otherwise the logical sequence would be lost. Waters (27), Hey (28), and other investigators who were concerned with free-radical chemistry had shown that diazo compounds produce organometallic compounds via free radicals. Sandin, McClure, and Irwin (29) found a similar reaction, and proposed a similar mechanism for formation of diaryliodonium salts. The analogy enabled me and Makarova to draw the iodonium and diazonium investigations together. We were interested in whether conditions existed which would make both onium types decompose heterolytically, rather than homolytically. The tetrafluoroborates, in particular, seemed unable to display homolytic decomposition. This is because the reaction would lead to atomic fluorine. Indeed, diphenyliodonium tetrafluoroborate proved to be an excellent heterolytic arylating agent.

Thus  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ,  $\text{SPh}_2$ ,  $\text{SePh}_2$ , and a number of nitrogen-containing bases, when fused with  $\text{Ph}_2\text{IBF}_4$ , were phenylated, giving onium compounds in very good yields (30, 31). The phenylation of pyridine was especially effective; diphenyliodonium tetrafluoroborate arylated it (heterolytically) at the nitrogen exclusively to yield phenylpyridinium salts, while the corresponding chloride reacted homolytically and gave nothing but a mixture of pyridines C-phenylated at the nucleus (32).

Similarly, benzenediazonium tetrafluoroborate arylated pyridine, but homolytically, and produced a mixture containing  $\alpha$ - and  $\beta$ - rather than *N*-substituted compounds. Heterolytic arylation occurs with nitrobenzene or a phenyltrimethylammonium salt (30), giving the meta isomers, whereas the Gomberg arylation reaction gives a mixture in which the para isomer prevails. We explained this by assuming that the benzenediazonium cation might give the diazo species with pyridine or other Lewis bases, so that the reaction would be directed along the homolytic path.

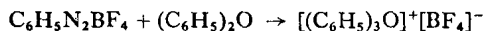
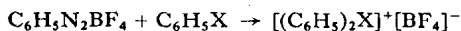


Like other diazonium salts, the tetrafluoroborates decomposed when treated with metal powders, and this process may resemble the above reaction.



This also explained the role of tetrafluoroborates and other complex anion salts in the organometallic syntheses described above.

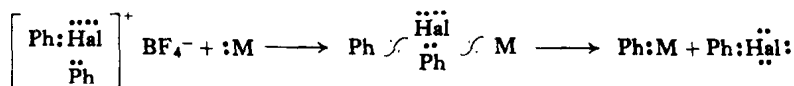
The most impressive result was the synthesis of diphenylbromonium tetrafluoroborate (30, 33, 34), diphenylchloronium tetrafluoroborate (30, 35), and triphenyloxonium tetrafluoroborate (30, 36) by decomposing benzenediazonium tetrafluoroborate in bromobenzene, chlorobenzene, and diphenyl ether, respectively (Nesmeyanov, Tolstaya, and Isaeva).



Spontaneous decomposition of  $\text{C}_6\text{H}_5\text{N}_2\text{HgBr}_3$  was also a source of diphenylbromonium salts (4). Diphenylbromonium and, especially, triphenyloxonium salts proved surprisingly stable towards electrophiles, and could be nitrated under drastic conditions to give the meta-substituted halogenonium and para-substituted oxonium cations (37). On the other hand, they arylated nucleophiles readily (38).

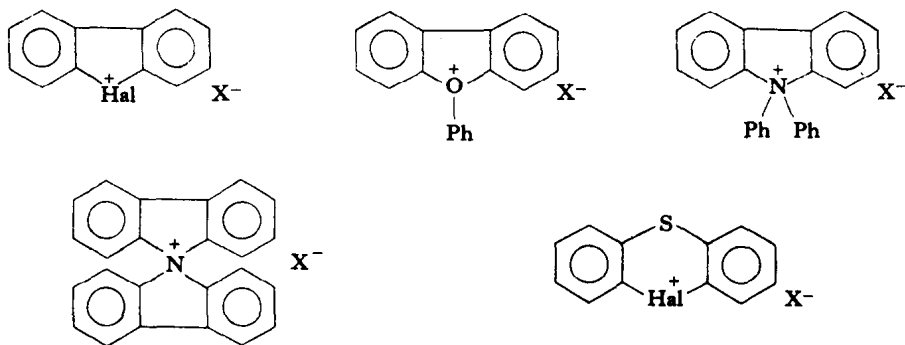
The halogenonium series  $\text{Ar}_2\text{Hal}(\text{X})$  and  $\text{ArAr}'\text{Hal}(\text{X})$  were synthesized and studied. They resembled iodonium salts very closely; for example, the respective iodides, when treated with Hg or Sn (but not Tl, Pb, Bi) powders, produced the organometallics in a yield up to 60% (39), in analogy with the reaction reported by Sandin, McClure, and Irwin (29) for diphenyliodonium salts.

Diphenylbromonium tetrafluoroborate gave 15% to 20% of the expected organometallics with Tl, Sn, Pb, Bi (but not Hg) powders (40). Perhaps, the better reactivity of the tetrafluoroborate as compared with the iodide may be explained in the same manner as with the diazonium arylation. This may be written as follows:

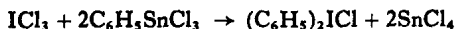


Noble metals such as Ag, Hg, and Pt do not react in this manner. Neither the iodide nor the tetrafluoroborate of the triphenyloxonium cation react with any of the metal powders, apparently because oxygen cannot expand its octet.

Thus, the diazonium synthesis of organometallic compounds had been extended to the onium synthesis, whatever its versatility and limitations. The analogy had to be completed and further extended. This was performed by my disciple O. A. Reutov and his co-workers (41), who showed that the salts  $\text{Ar}_2\text{IHgCl}_3$ ,  $(\text{Ar}_2\text{I})_2\text{SnCl}_6$ ,  $\text{Ar}_2\text{ISbCl}_4$ , and  $(\text{Ar}_2\text{I})_2\text{BiCl}_3$  gave satisfactory yields of the appropriate organometallics on reaction with metal powders (Reutov, Ptitsyna). Similar syntheses were achieved with diphenylbromonium and -chloronium salts, which yielded the derivatives of Hg, Tl, Sb, Sn, and Bi (40). Of course, the halogenonium method, unlike diazonium synthesis, can hardly be of preparative value, but this does not reduce its cognitive importance. Also, in collaboration with Tolstaya, Grib, and others, we studied the chemistry of onium compounds *per se*, and applied the heterolytic decomposition mentioned above to the synthesis of a number of heterocycles as shown in the accompanying scheme (42).



This short survey of our investigations on onium compounds is incomplete if we do not mention a novel synthesis of diaryliodonium salts discovered in collaboration with Freidlina (43);



and also work concerning Wittig "ate" complexes (44), performed in collaboration with Sazonova. We found possibly the simplest way to synthesize salts of the anion  $\text{BAR}_4^-$

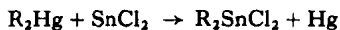


and obtained compounds where Ar is not only aryl but heterocyclic as well.

#### IV

### EARLY INVESTIGATIONS INTO ORGANOMETALLIC EXCHANGE REACTIONS

Now, I must refer to the early 1930s when the diazo method had allowed me to prepare various compounds of the type  $\text{Ar}_2\text{Hg}$  and  $\text{ArHgCl}$ . It seemed desirable to use these compounds for the synthesis of other organometallics. Together with my colleague K. A. Kocheshkov (45, 46), who had started his well-known organometallic research by studying organotin compounds, we discovered the reaction



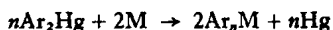
which proved to be a good way of obtaining organotin aromatics. In ethanol, if the Kharasch electronegativity of the radical R was sufficient, a side reaction occurred and an organometallic was not obtained.



In acetone the situation was somewhat better, but possibly because the acetone-enol was involved, the side reaction still sometimes predominated. In ligroin, however, though  $\text{SnCl}_2$  is hardly soluble in this solvent, all complications were avoided (47) and a number of organotin aromatics were synthesized and studied (46). Later the reaction was applied to the synthesis of chlorovinyl derivatives of tin (48). Organotin compounds of the type  $(\text{C}_2\text{H}_5)_2\text{Sn}$  or  $[(\text{C}_2\text{H}_5)_3\text{Sn}]_2$  were also able to abstract aromatic groups from mercury and thus give  $\text{Ar}_2\text{Sn}(\text{C}_2\text{H}_5)_2$  or  $\text{ArSn}(\text{C}_2\text{H}_5)_3$ , while the

reaction was the first source of organotin phenol or dimethylaniline derivatives (49). The compounds  $R_2TiX$  reacted with  $SnCl_2$  in an analogous manner and produced  $R_2SnCl_2$  and  $TiCl$  (50).

The organomercurials  $R_2Hg$  could also be used to obtain the organo derivatives of zinc (51), cadmium (52), and aluminum (53) *via* the exchange process



*Inter alia*, aromatic ring-substituted compounds  $Ar_2Zn$ ,  $Ar_2Cd$ , and  $Ar_3Al$  were prepared and their properties studied.

Another branch of the work was concerned with a reverse reaction, the interaction of mercury dichloride with organometallic compounds of Groups III, IV, or V. At that time, (1934), the literature on the reaction was surprisingly scarce.

It was found that mercury dichloride in neutral media readily abstracted phenyl groups from  $Ar_4Sn$ ,  $Ar_3SnCl$ ,  $Ar_2SnCl_2$ ,  $ArSnCl_3$ ,  $Ar_4Pb$ ,  $Ar_3PbCl$  (but not  $Ar_2PbCl_2$ ),  $ArSbCl_2$ , or  $Ar_2SbCl$ , and formed the  $ArHgCl$ .

In alkaline media all the above compounds, except for  $Ar_4Pb$  or  $Ar_2PbCl_2$ , formed  $Ar_2Hg$  almost instantaneously when treated with mercury dichloride (or mercuric oxide) (54). The compound  $ArB(OH)_2$  behaved similarly.  $RHgOH$  could be arylated in alkaline media in the same fashion; thus a new synthesis of unsymmetric  $RHgAr$  compounds was ready for use (Freidlina, Kocheshkov, Nesmeyanov) (55).

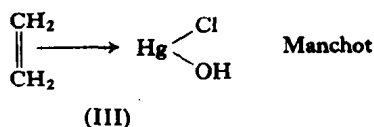
The arylation reactions described in this section were used not only synthetically but also for analysis of structures of "quasi-complex" compounds of mercury.

## V

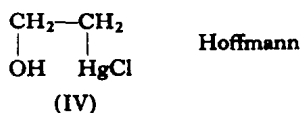
### QUASI-COMPLEX COMPOUNDS

Whoever is concerned with the organometallic chemistry of mercury cannot help admiring the striking compounds formed from olefins or acetylenes and mercuric salts, and the classical papers by K. Hoffmann, Schöller, Schraut, Kucherov, and their successors. Although the controversy as to the structures of the adducts, which had been discovered in 1920-1925, was not so sharp as before because increasingly evidence was accumulated in favor of a formulation with a mercury-carbon  $\sigma$ -bond, no one could forget the work of W. Manchot (56), who had been trying to show that the adducts might be, in modern notation,  $\pi$ -complexes. The

fact that acids or other reagents could produce  $\text{Hg}^{2+}$  and make the adducts lose olefin, made the adducts seem analogous to Zeise's salt, and raised the questions as to whether, for example, Hoffmann's ethanolmercurichloride should be formulated as

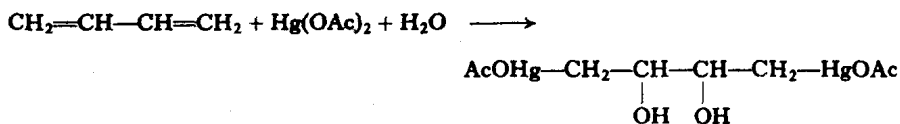


or as



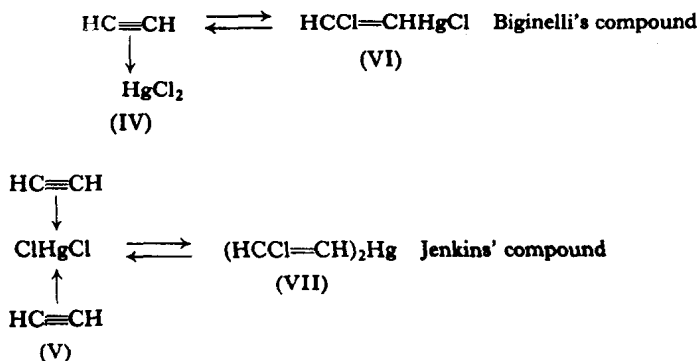
The first structure, if arylated by  $\text{C}_6\text{H}_5\text{SnOOH}$  in alkaline medium according to the procedure developed by us [see above (55)], should lead to diphenylmercury and ethylene, while the second structure should give the unsymmetrical organomercurial  $\text{HOCH}_2\text{CH}_2\text{HgC}_6\text{H}_5$ .

In reality, the second possibility occurred (57), and the same was true for the adducts containing other olefins. Finally, we verified the presence of hydroxyl in structure (IV) through reaction with phenyl isocyanate. Thus, the convincing experiments of Hoffmann, Middleton, and R. Adams were confirmed by our decisive evidence, so that  $\pi$ -structures were condemned to fade from the scene for these compounds. However, to emphasize the behavioristic similarity with the  $\pi$ -complexes, I suggested the term "quasi-complex" for the compounds which are formed from metallic salts and olefins or acetylenes through addition to the  $\pi$ -bond. A number of such quasi-complex compounds were obtained and studied by us. In particular, we showed that butadiene or its homologs, contrary to the earlier opinion of Sand, also formed the quasi-complex adducts in water, e.g.,



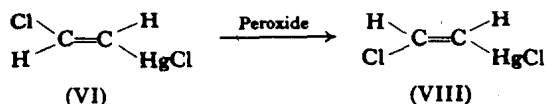
Other adducts were also prepared, namely, those of allylcyclopentane, 2-allyldecalin, diallyl ether, and diallylamine. The latter three compounds are oxygen or nitrogen-heterocycles. They all are quasi-complexes [Nes-mayanov, Lutsenko (58, 59)].

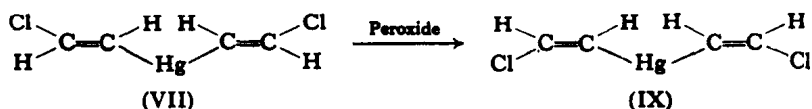
With the adducts from mercury dichloride and acetylene, we [Nesmeyanov, Freidlina, Borisov (60-62)] began the investigation by studying the compounds of Biginelli and Jenkins for which either  $\pi$  or  $\sigma$ -structures, or tautomerism between these might be assumed.



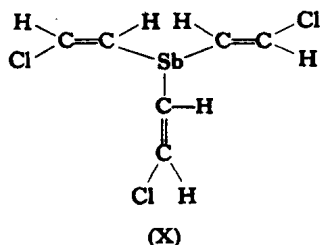
Here, the action of  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , or even of such a complexing agent as  $\text{PPh}_3$ , led to the elimination of the mercury salt and the quantitative formation of acetylene. In addition, our method of phenylation with  $\text{PhSnOOH}$  produced diphenylmercury and acetylene.

This seemed to establish the  $\pi$ -complex nature of the compounds. Other reactions, however, suggested the organometallic chlorovinyl structures, e.g., the reaction with iodine leading to iodochloroethylene, or the transfer of chlorovinyl from one metal to another, described more extensively below. This raised a question: Were, perhaps, the complex and the chlorovinyl species tautomers of a new kind, i.e., could there be an equilibrium isomerism of the type  $(\text{IV}) \rightleftharpoons (\text{VI})$  and  $(\text{V}) \rightleftharpoons (\text{VII})$ ? Our final answer was, No. In other words, the chlorovinyl structures (VI) and (VII) were correct and tautomerism was absent. Actually, we found that (VI), (VII), (VIII), and (IX) existed as geometric isomers, the isomers (VI) and (VII) having a trans configuration while (VIII) and (IX) had a cis configuration. The compounds strictly retain their configurations when dissolved in various solvents in the absence of light or peroxides, so that tautomerism is ruled out.





The *cis* isomers are more stable than the *trans* isomers, so they may be prepared from the *trans* compounds by treating with peroxides or on irradiation (63, 64). Moreover, *cis*-chlorovinylmercury chloride could be obtained from acetylene and mercury dichloride vapors [Freidlina, Nogina (65)] and symmetrized by ammonia to give (IX), which retained the initial configuration (66). Finally, *cis*-chlorovinylmercury chloride could be synthesized from mercury dichloride and acetylene.



This reaction produced a mixture of (VI) and (VIII) from which pure (VIII) was isolated (67).

The compounds (VIII) and (IX) display their quasi-complex properties less clearly than do (VI) and (VII). Their *trans* isomers lose acetylene much more easily than do the *cis* ones.

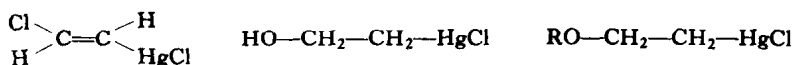
We [together with Borisov (68)] prepared chlorovinyl compounds of antimony by saturating  $\text{SbCl}_3$  with acetylene, distilling off  $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$ , and reducing the distillate to  $(\text{ClCH}=\text{CH})_3\text{Sb}$  (X). This procedure afforded pure *trans*-( $\text{ClCH}=\text{CH}$ ) $_3\text{SbCl}_2$  as well as the *cis-trans* species (X) [from  $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$ ], which was initially thought to be a pure *cis* form. All these compounds are also of the quasi-complex type.

In other studies, with N. K. Kochetkov (69, 70), we obtained the compounds  $\text{R}(\text{Cl})\text{C}=\text{C}(\text{HgCl})\text{R}'$  from the appropriate acetylenes. Quasi-complex elimination of the  $\text{RC}\equiv\text{CR}'$  was especially easy, just by treating with sodium chloride in cold water, when R or R' were carboxyl groups.

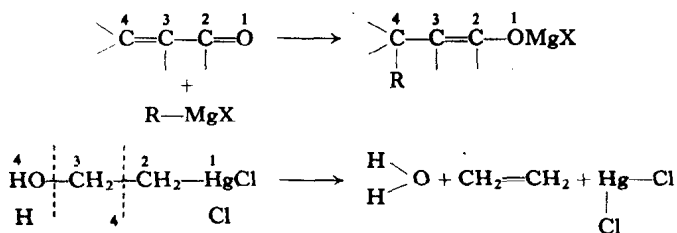
Why do quasi-complex compounds liberate acetylene or olefin so



readily? The answer was as follows [Nesmeyanov, Freidlina, Borisov (60, 71)]. The polarizability of Hg—C bonds shows its effect in these compounds:



The positions of the Cl—C, HO—C, and RO—C bonds allows them to conjugate with the Hg—C bond (“ $\sigma, \sigma$ -conjugation”). Hence, an electrophile (with the latter two substrates), or an agent which can bind  $\text{Hg}^{2+}$ , or a reagent which combines both properties, such as HCl, will break the conjugated  $\sigma$ -bonds, create at the center of the molecule the new  $\pi$ -bond, and eliminate olefin or acetylene. This is formally similar to the 1,4-addition occurring in  $\pi, \pi$ -conjugated systems.



The 1,2 and 3,4 bonds are broken, the atoms 1 and 4 add fragments of a reagent, and the new  $\pi$ -bond, positioned between carbon atoms 2 and 3, appears. However, a  $\pi, \pi$ -conjugated molecule does not lose its integrity, whereas the  $\sigma, \sigma$ -conjugated system undergoes the rupture of its 1,2 and 3,4  $\sigma$ -bonds, with elimination of the central fragment. The analogy would be more than simply formal if both reactions involved a cyclic transition state, but this was never verified. Thus, we established the concept of the “quasi-complex” compound, characterized by a pronounced  $\sigma, \sigma$ -conjugation. This led to a better understanding of the peculiar reactivity of  $\sigma, \pi$ -conjugated systems as well (71, 72).

## VI

### INVESTIGATION OF THE GRIGNARD REACTION

This research commenced with the same motive as that discussed in the preceding section. Namely, were the products arising from the Grignard alkylation of oxo compounds  $\pi$ -complexes or, as suggested by Grignard,