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RESEARCH OF A. N. NESMEYANOV ON ORGANOMETALLIC COMPOUNDS

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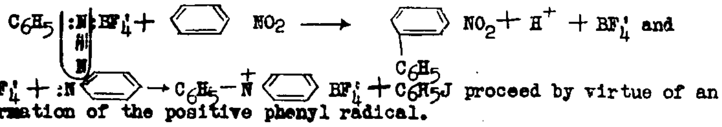
/A Digest/

The following is a review of research done by Academician Aleksandr Nikolayevich Nesmeyanov in the field of organometallic compounds. The introduction of mercury into a definite position of the aromatic nucleus (over the diazonium salt--mercuric chloride complex) is discussed and the reactions $Ar\text{-}N{=}N\text{-}COOK + HgCl_2 \rightarrow ArHgCl + N_2 + CO_2 + KCl$ and $4CHN_2.COOC_2H_5 + 3HgCl_2 \rightarrow 2CH_2ClCOOC_2H_5 + 4N_2 + Hg\,[C.Cl(HgCl)COOC_2H_5]_2$ are mentioned in that connection.

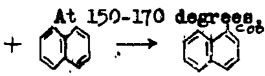
Several reactions of the types $(RN_2Cl)_2.SnCl_4 + 2Zn \rightarrow R_2SnCl_2 + 2N_2 + 2ZnCl_2$, $C_6H_5N_2Cl.PbCl_2 + Cu \rightarrow (C_6H_5)_2PbCl_2$, $4C_6H_5N_2BF_4 + 3Pb \rightarrow (C_6H_5)_4Pb + 4N_2 + 2Pb(BF_4)_2$, $C_6H_5N_2Cl.SbCl_3 + Zn \rightarrow C_6H_5SbCl_2 + N_2 + ZnCl_2$, $3(XC_6H_4N_2Cl)_2.BiCl_3 + 4Bi \rightarrow 2(XC_6H_4)_3Bi + 6N_2 + 5BiCl_3$, $(C_6H_5)_2Hg + 4N_2O_3 \rightarrow 2C_6H_5N_2NO_3 + Hg(NO_3)_2$ are listed, and the great number of conversions and variations based on the typical reactions is pointed out.

Reactions



proceed by virtue of an intermediate formation of the positive phenyl radical.

At 150-170 degrees, trichloracetic acid reacts with naphthalene: $Cl_3C.C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$ + (yield 3 percent)



This is explained by the following scheme:

a. $CCl_3{:}\,\{\,C\begin{smallmatrix}\nearrow O\\ \searrow O{:}\end{smallmatrix}\,\{\,H \longrightarrow CCl_3{:} + CO_2 + H^+$

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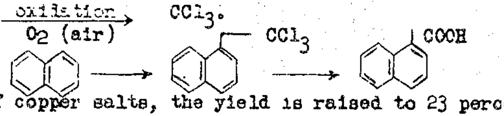
b. $CCl_3: + H^+ \longrightarrow CHCl_3$

c. $CCl_3: \xrightarrow[O_2\ (air)]{oxidation} CCl_3\cdot$

d. $CCl_3\cdot$ +



In the presence of copper salts, the yield is raised to 23 percent; the oxidation (stage c) proceeds over the cupric ion, and is facilitated thereby.

The reaction $RJO_2 + HgO \rightarrow RHg^+ + JO_3'$ proceeds with a yield of 80-90 percent in the presence of silver oxide.

Mercuric chloride can be arylated in the following manner: $(C_6H_5)_4Sn + HgCl_2 \rightarrow (C_6H_5)_3SnCl + C_6H_5HgCl$; $(C_6H_5)_2SnCl_2 + 2HgCl_2 \rightarrow 2C_6H_5HgCl + SnCl_4$ $C_6H_5SnCl_3 + HgCl_2 \rightarrow C_6H_5HgCl + SnCl_4$

This reaction has been applied extensively to organic compounds of lead, arsenic, and antimony.

In an alkaline medium two aryls become attached to the mercury atom: $(C_6H_5)_2SnO + HgO + 2NaOH \rightarrow (C_6H_5)_2Hg + Na_2SnO_3 + H_2O$

Similarly, organomercuric hydroxides can be arylated: $RHgOH + R'SbO + NaOH \rightarrow RHgR' + NaSbO_2 + H_2O$

Compounds RHgR' containing functional groups in the aromatic nuclei can be obtained in this manner; this would be impossible if organomagnesium compounds were used.

The reaction of a series of symmetric organomercuric compounds (which became available via the diazo compounds) with metallic zinc or aluminum proceeds in the following manner:
$(ClC_6H_4)_2Hg + Zn \rightarrow (ClC_6H_4)_2Zn + Hg$, $[(CH_3)_2NC_6H_4]_2Hg + Zn \rightarrow [(CH_3)_2NC_6H_4]_2Zn + Hg$.

These reactions have been studied by Nesmeyanov's collaborators. It is essential to understand that while conversions of the type $R_2Hg + SnCl_2 \rightarrow R_2SnCl_2 + Hg$ can be carried out with Grignard reagents, the latter are much more reactive than mercuric compounds and affect the substituents in aromatic nuclei. In the presence of certain radicals, the following variation occurs: $R_2Hg + SnX_2 + 2C_2H_5OH \rightarrow 2RH + Hg + (C_2H_5O)_2SnX_2$.

The relative facility of this conversion enables one to measure the affinity of various radicals to hydrogen, i. e., the electronegative strength of these radicals. It could be shown that organomercuric salts react with anhydrous $SnCl_2$ in accordance with the equation $2RHgCl + 2SnCl_2 \rightarrow R_2SnCl_2 + 2Hg + SnCl_4$, while the conversion $RHgX + SnX_2 \rightarrow RSnX_3 + Hg$ plays a subordinate role. With bromides another variation occurs: $2RHgBr + SnBr_2 \rightarrow R_2SnBr_2 + 2HgBr$.

Thus a whole series of compounds R_2SnX_2 and $RSnX_3$ (the latter after a reaction with SnX_4) containing halogen in the aromatic nucleus could be obtained. To synthesize compounds containing a dimethylamino or hydroxyl group in the nucleus, the variation expressed in the following equation was found useful: $[p\text{-}(CH_3)_2NC_6H_4]_2Hg + [(C_2H_5)_3Sn]_2 \rightarrow 2p\text{-}(CH_3)_2NC_6H_4Sn(C_2H_5)_3 + Hg$.

This method made possible the synthesis of compounds of the type $ArSnAlK_3$ and Ar_2SnAlK_2 containing any desired substituent in the aromatic nucleus.

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About 15 years ago Nesmeyanov and his group of workers launched an extensive investigation of addition compounds of metal halides and unsaturated compounds. Compounds of this type behave either as molecular complexes or as products of addition to a triple bond, i. e., Cl-CH=CH-HgCl. This dual character has led to doubts and controversy on the subject of the actual constitution of substances of this class. The work of Nesmeyanov and his collaborators has permitted a solution of that question. The essential similarity of chemical behavior could be established on the basis of accumulated data in the new field of quasi-addition complexes. Trans-ClCH=CHHgCl, trans-$(ClCH=CH)_2Hg$, cis-ClCH=CHHgCl, and cis-$(ClCH=CH)_2Hg$ have been adequately characterized. These four substances are definitely δ-chlorovinyl organomercuric compounds, as the following reactions, which lead to compounds containing the δ-chlorovinyl group, show quite clearly.

$$
ClCH{=}CHHgCl \left\{ \begin{array}{l} \xrightarrow{Cl_2} ClCH{=}CHCl + HgCl_2 \\ \xrightarrow{Br_2} ClCH{=}CHBr + HgCl.Br \\ \xrightarrow{J_2} ClCH{=}CHJ + HgClJ \\ \xrightarrow{JCl_3} ClCH{=}CHJCl_2 + HgCl_2 \end{array} \right.
$$

$$
(ClCH{=}CH)_2Hg \left\{ \begin{array}{l} \xrightarrow{HgCl_2} 2ClCH{=}CHHgCl \\ \xrightarrow{JCl_3} ClCH{=}CHJCl_2 + ClCH{=}CHHgCl \\ \xrightarrow{ClCH=CHJCl_2} (ClCH{=}CH)_2JCl + ClCH{=}CHHgCl \\ \xrightarrow{SnCl_2} (ClCH{=}CH)_2SnCl_2 + Hg \\ \xrightarrow{Pb(CH_3COO)_4} \begin{matrix} (ClCH{=}CH)_2 \\ (OCOCH_3)_2 \end{matrix}\!>\!Pb + (CH_3COO)_2Hg \\ \xrightarrow{Cl_2} ClCH{=}CHHgCl + ClCH{=}CHCl \end{array} \right.
$$

In another type of reaction, decomposition into acetylene and mercuric chloride occurs. This decomposition can be brought about by heating above the melting point of the highest melting of the four compounds (124 degrees) $(ClCH=CH)_2Hg \longrightarrow ClCH=CHHgCl + C_2H_2$, $ClCH=CHHgCl \longrightarrow HgCl_2 + C_2H_2$.

The action of reagents capable of binding mercuric chloride induces the same type of decomposition even at room temperature $C_2H_2Hg\begin{matrix}Cl\\Cl\end{matrix} + 3KJ \rightarrow C_2H_2 + \left[J\overset{J}{\underset{J}{Hg}}\right]K + 2KCl$

Silver oxide in water converts trans- δ-chlorovinyl mercuric chloride into the soluble hydroxide ClCH=CHHgOH. The latter is capable of forming a number of salts with various acids. Among these the phthalimide salt merits attention. The salts in question could be also obtained in the following manner: $(ClCH=CH)_2Hg + HgJ_2 \longrightarrow 2ClCH=CHHgJ$.

Similar conditions obtain in a series of chlorovinyl compounds of other metals. Thus, cis and trans $(ClCH=CH)_3SbCl_2$ and cis and trans $(ClCH=CH)_3Sb$ have been synthesized and found to behave in the following manner:

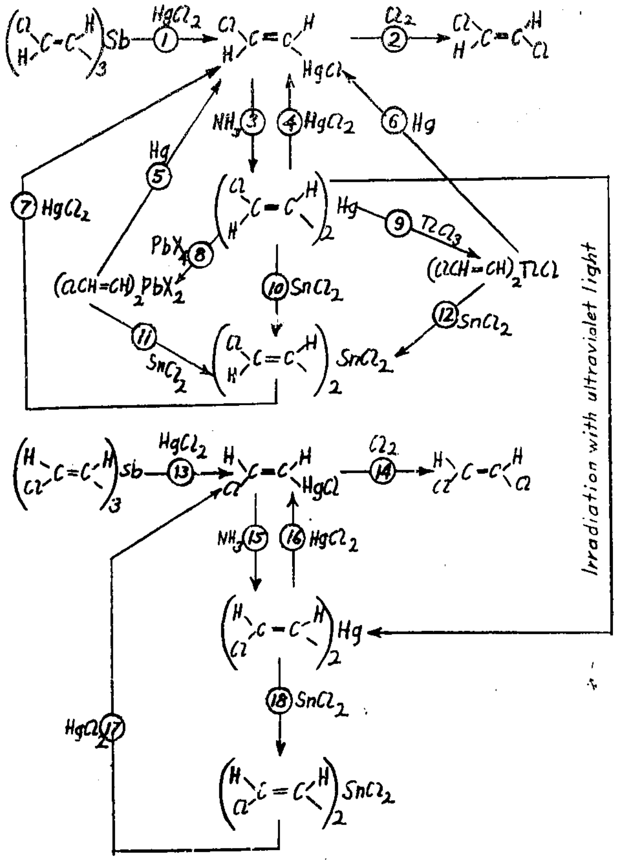
$$
(ClCH{=}CH)_3SbCl_2 \left\{ \begin{array}{l} \xrightarrow{2J_2} 3ClCH{=}CHJ + SbCl_2J \\ \xrightarrow{3Br_2} 3ClCH{=}CHBr + SbCl_2Br_3 \\ \xrightarrow{Na_2S_2O_4} (ClCH{=}CH)_3Sb \end{array} \right.
$$

$$
(ClCH{=}CH)_3Sb + 3HgCl_2 \rightarrow 3ClCH{=}CHHgCl + SbCl_3
$$

The chlorovinyl compounds of tin, lead, and thallium react in an analogous manner.

The products of the addition of mercury salts to olefins or carbon monoxide must be also regarded as belonging to the class of quasi-complex compounds. In all compounds of this class the mercury is exceptionally mobile, i.e., it approaches the ionic state more closely than in ordinary mercury compounds. This is due to conjugation in which the mercury atom participates.

It could be shown that the transfer of the chlorovinyl group proceeds under rigid retention of its steric configuration in all reaction involving electrophilic and radical substitution at the olefin carbon. This is illustrated by the following scheme:



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This retention of the configuration is also observed in the reaction

which leads to cis-omega-chlorostyrenes. The synthesis of these rather inaccessible compounds has been facilitated by that reaction.

A general rule to the effect that electrophilic and radical substitutions at a carbon bound by means of a double bond to another carbon proceed under retention of the geometric configuration has been formulated on the basis of the experimental data obtained by Nesmeyanov and his collaborators. This rule is of considerable theoretical interest and undoubtedly has an important bearing on substitutions in aromatic nuclei.

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