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METALLOTROPY AND DUAL REACTIVITY

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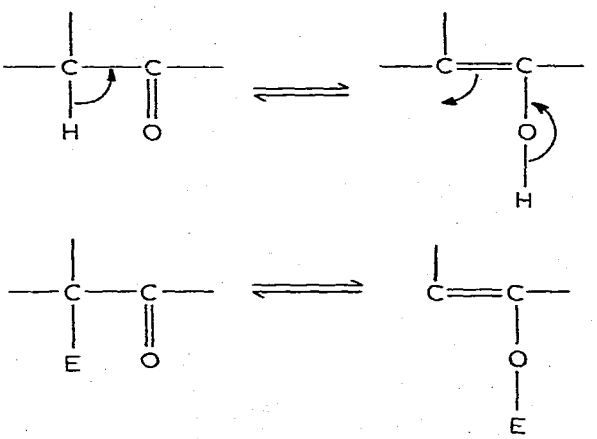
There are two types of metallo (or elemento) derivatives of enolic compounds:



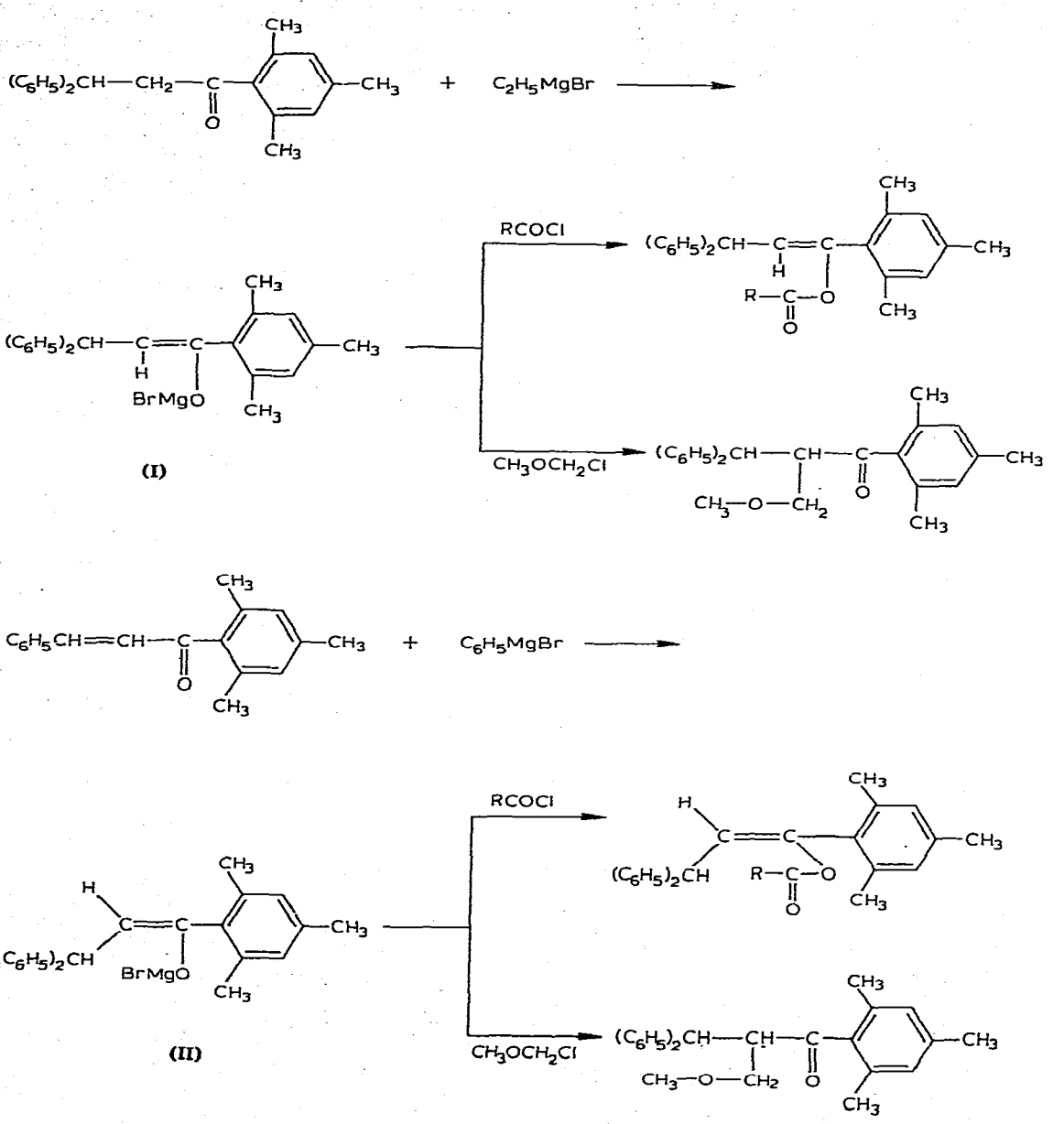
where E denotes the atom of an element or an alkylelemento group such as, for example, C_2H_5Hg and $(C_2H_5)_3Pb$. Such pairs can be interconverted by reversible or irreversible rearrangement, and σ,π-conjugation of linkages similar to that observed in keto-enols themselves can occur. These features make the above types of compounds, which are the primary topic of the present article, akin to E-derivatives of other tautomeric structures which are also dealt with below.

First, we consider the structures $-\overset{|}{C}=\underset{|}{C}-$ (OE). By treating mercury diacetaldehyde with lithium we, in collaboration with Lutsenko, isolated a lithium derivative of acetaldehyde which, according to all its properties, represents the simplest enolate [1].

$$Hg(CH_2-\underset{\|}{C}-H)_2 \xrightarrow{Li} CH_2=\underset{|}{C}-H + Hg$$
$$\qquad\qquad O \qquad\qquad\quad OLi$$

Before isolating this simplest example of an enolate we, in collaboration with

Sazonova [2], investigated BrMg-enolates of diphenylpropiomesitylene, which were obtained in two-crystalline stable stereoisomeric forms.

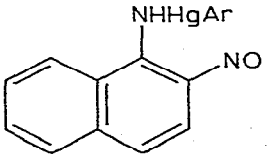


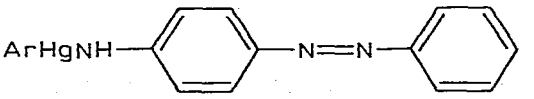
The two stereoisomers, denoted I and II, do not undergo interconversion. When acylated, each forms the corresponding enol acylate. In reaction with CH_3OCH_2Cl, the same CH_3OCH_2C-ketone derivative is formed in both cases together with the CH_3OCH_2O-enolate of retained configuration. It is significant that BrMg-enolates I and II when alkylated (CH_3OCH_2 being regarded as "alkyl") form one and the same "ketone" while at the same time giving different stereoisomeric CH_3OCH_2O-enol derivatives. As the two enolates I and II

are not converted into each other, it is impossible to transform each of them into a tautomer of ketonic structure, otherwise mutual conversion of stereoisomers would have been possible. Thus, the formation of CH_3OCH_2C-ketone does not proceed through the absent ketone tautomer, and each of the BrMg-enolates I and II reacts with CH_3OCH_2Cl to form the same ketone and the two stereoisomeric CH_3OCH_2O-enols.

Hückel once made a statement to the effect that the concept of tautomerism in the case of metallo-derivatives of tautomeric systems is irrelevant, and should be replaced by the concept of anion mesomerism. In my papers with Sazonova [2] it was shown by study of α-metal carbonyl compounds that the metallo-derivatives of the tautomeric systems can have structures with fixed rather than delocalized bonds when the metal involved gives rise to rather low polarities. In this connection, an investigation of the structures of organometallic derivatives of tautomeric and potentially tautomeric systems containing hetero-atoms as cation-acceptor centres was undertaken in the Laboratory of Organometallic Compounds of the Institute of Organo-Element Compounds. In the systems investigated the potential ambivalent anion is associated with a univalent organometallic group of the R_nM type containing such heavy non-transition metals as mercury, tin or lead. The groupings RHg, R_3Sn or R_3Pb were used as models because of the relatively low polarity of the bonds formed by them. Spectral methods were used for the investigation.

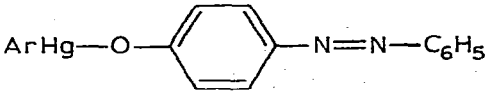
The most detailed study was made of arylmercury derivatives of the tautomeric and potentially tautomeric systems. It was established that within the limits of sensitivity of the spectral methods, the organometallic derivatives in solution in most cases exist in only one of the two possible isomeric forms, matching, as a rule, the structure of the corresponding hydrogen compounds. Thus, the UV and visible spectra of *p*-dimethylaminophenylmercury derivatives of nitrosoanilines and aminoazo compounds in solution show that the nitroso and aminoazo structures, respectively, are present [3,4]:



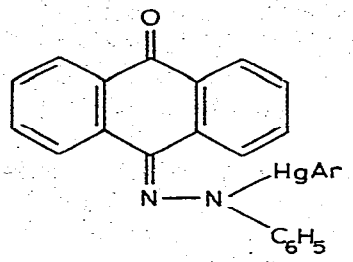


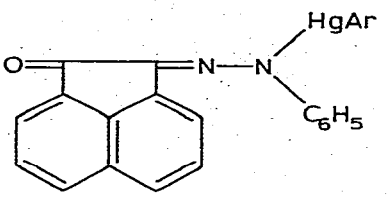
(Ar = 4-$(CH_3)_2NC_6H_4$ here and subsequently)

Similar derivatives of the oxyazo compounds of the benzene series exist in the azo form in solution and the crystal:



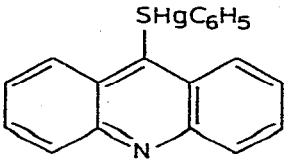
In contrast the derivatives of phenylhydrazones of anthraquinone and acenaphthenequinone have a hydrazone structure:

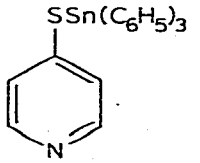




which corresponds to the structure of the free compounds [5].

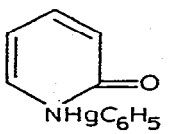
The largest difference in the structure of the organometallic derivatives and the corresponding potentially tautomeric prototropic systems were observed with oxy- and mercapto-N-heterocycles and their acyclic analogues. Thus, UV spectra show that the C_6H_5Hg derivatives of thioamides and 9-thioacridone, and the C_6H_5Hg, $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of 4-thiopyridone are S-derivatives [6,7]:

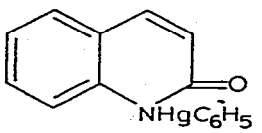




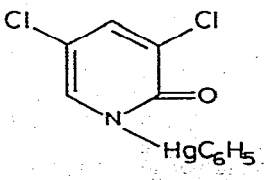
in contrast to the free compounds, which have a thione structure. This behaviour is probably to be associated with the greater "softness" of organometallic cations compared with the proton.

Again, the C_6H_5Hg derivatives of 2-pyridone and 2-chinolone are N-derivatives [7]:

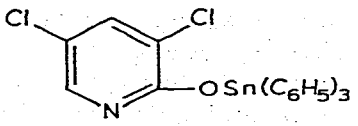


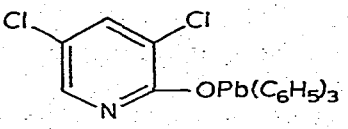


Although in this case the corresponding free compounds are also N-derivatives, the creation of steric hindrance by introducing the methyl group into position 8 of chinolone does not change the structure of the C_6H_5Hg derivative from lactam to lactim. 3,5-Dichloro-2-pyridone and its derivatives were used to demonstrate the difference in the behaviour of the groups $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ on the one hand, and C_6H_5Hg, on the other, in the lactim—lactam tautomeric system. It turned out that the C_6H_5Hg derivative has a lactam structure:

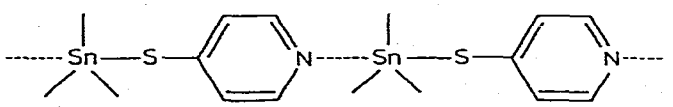


whereas the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives exist in the O-form:

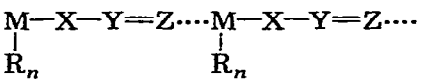




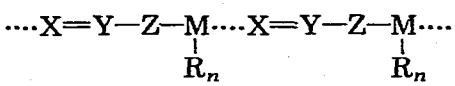
The IR spectra of the C_6H_5Hg derivatives of oxy-N-heterocycles and certain amides indicate that there is intermolecular coordination between the C_6H_5Hg group and the oxygen of the carbonyl group [7]. Similarly, Mössbauer spectral data point to extensive intermolecular coordination between the organotin group and the heterocyclic nitrogen atom in the crystals of the oxy- and mercapto-N-heterocyclic derivatives, e.g. [8]:



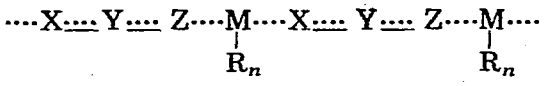
The extensive intermolecular coordination between the organometallic group and the second cation-acceptor centre of the tautomeric system which occurs in the crystal can give rise to considerable uncertainty in defining the nature of the structure of these compounds in the crystalline state. This is due to the fact that in the general case of organometallic derivatives of the tautomeric systems with hetero-atoms at the ends, intermolecular coordination of the type:



brings the above mentioned structure closer to the isomeric one:



so that in principle the real structure in the crystal may be rather close to a resonance hybrid between the specified extreme forms:

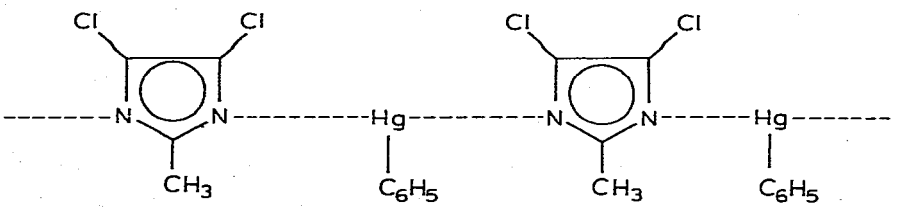


As a result, a state of intermolecular mesomerism arises in which the organometallic group is connected to the two cation-acceptor centres of the tautomeric system to approximately the same extent. In consequence, the problem of the structure of the compound in the crystal cannot be solved unambiguously in a number of cases even with the help of the X-ray structural analysis. An example of a case in which this problem was solved is provided by the $(C_6H_5)_3Sn$ derivative of 4-thiopyridone, for which an X-ray study confirmed, that, in spite of extensive intermolecular coordination, the structure is that of the S-derivative [9].

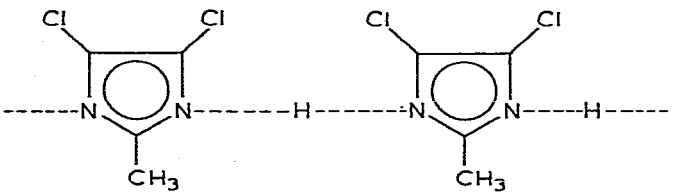
The intermolecular mesomerism of the organometallic derivatives of the tautomeric and potentially tautomeric systems disappears in most cases on going from the crystal to a highly dilute solution in an inert solvent or to a solution in a solvating solvent in which there are no self-associative interactions between the molecules of the compound. Thus, in solution the question of the structure of the organometallic derivatives of tautomeric systems containing bonds of low-

polarity between the metal and the cation-acceptor centres is capable of a definite answer, as shown by the spectral investigations mentioned above.

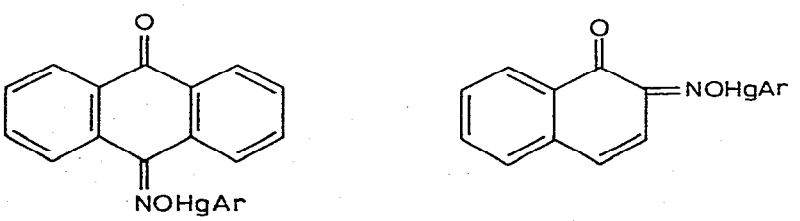
At present, in the light of the asymmetry of the hydrogen bonds, the structures of prototropic tautomeric systems in the crystal are generally discussed in terms of separately existing discrete tautomers. It is thus noteworthy that because of more intense intermolecular coordination, intermolecular mesomerism is more characteristic of organometallic derivatives than of prototropic tautomeric systems. For example, ^{35}Cl NQR data reveal that the structure of the C_6H_5Hg derivative of 4,5-dichloro-2-methylimidazole in the crystal more closely resembles the fully delocalized bond structure [10]:



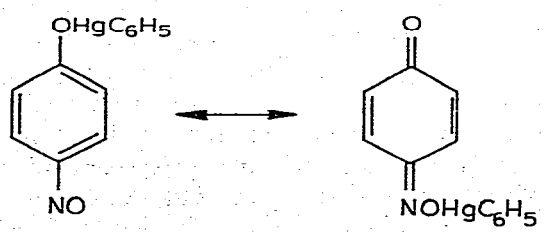
than the structure of the hydrogen compound resembles the delocalized hydrogen-bond structure:



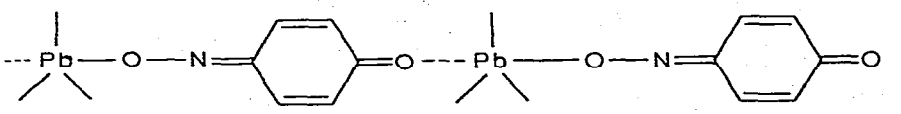
Interesting results were obtained for the organometallic derivatives of nitrosophenols [11-12]. Thus, studies of the visible and IR spectra of arylmercury derivatives of nitrosophenols of the naphthalene and anthracene series established that in the solution and the crystal they have a quinoneoxime structure:



In contrast, the derivatives of the nitrosophenols of the benzene series, which also exist in the crystal in a quinoneoxime form, exist in solution as an equilibrium mixture of the nitrosophenol and quinoneoxime form, with the latter predominating:



The position of the equilibrium depends on the nature of the solvent, the substituents in the nitrosophenol ring and the temperature, and is independent of the nature of the arylmercury radical. This was the first clearly established case of metallotropic equilibrium for organometallic derivatives of tautomeric systems. Later similar behaviour was observed with the $(C_6H_5)_3Sn$ and $(C_6H_5)_3Pb$ derivatives of *p*-nitrosophenol and its substituted analogues for which the amount of the nitroso form increases in going from chloroform to tetrahydrofuran and pyridine. For compounds of this type in benzene solution the formation of coordinatively-associated systems was demonstrated, the association being broken down by addition of pyridine. An associated quinoneoxime structure for such compounds in the crystalline state was indicated by the IR spectra:

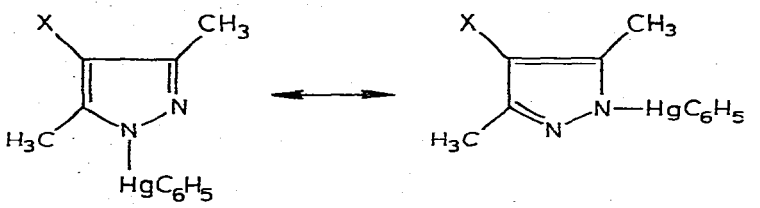


It was established that the introduction of a substituent with an unshared electron pair into the 2-position of the nitrosophenol ring results in a larger amount of the nitroso form for the C_6H_5Hg derivative than for the $(C_6H_5)_3Pb$ and $(C_6H_5)_3Sn$ derivatives and the hydrogen analogue, which is consistent with the fact that the C_6H_5Hg group has a greater ability to engage in intramolecular coordination [13].

The existence of tautomeric equilibrium of aminopyridine and pyridonimine forms was established by UV spectra for solution of the C_6H_5Hg derivatives of 2- and 4-arylsulphonylaminopyridines [14-15]. The amount of the pyridonimine form increases with an increase in the polarity and the coordinating capacity of the solvent; and for the C_6H_5Hg derivative in most solvents the aminopyridine form is more stable than for the hydrogen compounds, and this is clearly due to intramolecular coordination between the C_6H_5Hg group and the heterocyclic nitrogen atom and/or the oxygen atom of the sulphonyl group. A linear relationship between pK_T and the Hammett σ constants of substituents in the phenylsulphonyl group shows that polar factors have similar effects on the position of the tautomeric equilibrium for the arylsulphonylaminopyridines and their C_6H_5Hg derivatives.

In cases of metallotropic tautomerism considered above, in which the migration of an organometallic group takes place between like hetero-atoms, are characterized by high speeds of tautomeric conversions, which makes study of their structure in solution at room temperature by the NMR technique very difficult; for example, it has recently been established that for the $(C_2H_5)_3Sn$ and $(C_6H_{11})_3Sn$ derivatives of *p*-nitrosophenol the interconversion of the tautomeric forms is a rapid process on the PMR time scale at room temperature. Going to lower temperatures for solutions in THF leads either in extensive association, giving rise to intermolecular mesomerism, or to a complete displacement of the equilibrium in favour of the quinoneoxime form [16]. Therefore, in the case of organometallic derivatives of tautomeric systems with hetero-atoms as the cation acceptor centres, the NMR method can be most successfully used for investigating the so-called symmetric systems. An example of such a system is provided by the C_6H_5Hg derivatives of 4-substituted 3,5-dimethylpyrazols, for which

temperature-variable PMR established the occurrence of metallotropic conversions [17]:



which appear to occur mainly by the intermolecular mechanism. Unfortunately, with these model compounds it was not possible to compare the rates of the metallotropic and prototropic tautomeric conversions. At the same time, the higher migratory ability of the C_6H_5Hg and $(C_6H_5)_3Pb$ groups as compared to hydrogen in intermolecular exchanges in some NH and SH acids and their organometallic derivatives [18-19] allows us to assume that the metallotropic conversions in tautomeric systems with heteroatoms as the cation-acceptor centres can proceed at a higher rate than the prototropic conversions, the former being accompanied by extensive intermolecular exchange.

Along with many other types of organometallic compounds, α-metallated carbonyl compounds were virtually unavailable for many years.

The discovery of the general methods of synthesizing such compounds and investigation of their chemical behaviour were carried out at the Moscow University by me and my collaborators, partly with me and partly with their own coworkers [20-35]. In this work the first methods for obtaining metallated aldehydes and ketones were developed, starting from ethers or esters of enolic forms of carbonyl compounds:

$$CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}OR' + HgX_2 + H_2O \rightarrow XHgCH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R + R'OH + HX$$

$$CH_2{=}\underset{\displaystyle OCOR'}{\underset{|}{C}}{-}R + R''_3SnOR \rightarrow R''_3SnCH_2\underset{\displaystyle O}{\underset{\|}{C}}{-}R + R'COOR$$

and α-metallated derivatives of carbonic acids were made from ketenes:

$$2CH_2{=}C{=}O + HgX_2 + 2R'OH \rightarrow Hg(CH_2COOR')_2 + 2HX$$

$$Hg(CH_2\underset{\displaystyle O}{\underset{\|}{C}}{-}R)_2 + 2CH_2{=}C{=}O \xrightarrow{R'OH} Hg(CH_2COOR')_2$$

$$\xrightarrow{H_2O} Hg(CH_2COOH)_2$$

$$\xrightarrow{C_6H_6} Hg(CH_2COO\underset{\displaystyle R}{\underset{|}{C}}{=}CH_2)_2$$

$$R_3SnOR' + CH_2{=}C{=}O \rightarrow R_3SnCH_2COOR'$$

$$Cl_3GeOCH_3 + CH_2{=}C{=}O \rightarrow Cl_3GeCH_2COOCH_3$$

$$R_3SiNR'_2 + CH_2{=}C{=}O \rightarrow R_3SiCH_2CONR'_2$$

$$R_3EH + CH_2{=}C{=}O \xrightarrow{h\nu} R_3E\underset{\displaystyle O}{\underset{\|}{C}}CH_3 \quad (E = Ge, Sn)$$

etc.

The yields are usually in the 70-90% range.

Further development of these investigations consisted of extending the

methods for the transfer of the moieties containing functional groups from one organoelement compound to the other by use of organoelement halides, hydrides, sulphides, etc., which increased the range of available functionally-substituted organoelement compounds and led to the preparation of novel types of organic compounds of P, As, Sb and other elements [36-42]:

$$Hg(CH_2COOR)_2 + R'_3EH \rightarrow R'_3ECH_2COOR + Hg + CH_3COOR \quad (E = Ge, Sn)$$
$$Hg(CH_2COOCH_3)_2 + (C_2H_5)_3SnSn(C_2H_5)_3 \rightarrow 2(C_2H_5)_3SnCH_2COOCH_3 + Hg$$
$$Hg(CH_2COOCH_3)_2 + (R_3Sn)_2S \rightarrow 2R_3SnCH_2COOCH_3 + HgS$$
$$R_3SnCH_2COOCH_3 + R'_3GeX \rightarrow R'_3GeCH_2COOCH_3 + R_3SnX$$

With the α-metallated carbonyl compounds, two clearly defined features can be observed, namely the unusually high reactivity compared with alkyl and aryl derivatives and the occurrence of two distinct reactions, one involving transfer and the other retention of the reaction centre [43-45]:

$$Hg(\overset{1}{C}H_2-\overset{2}{C}\overset{3}{\underset{OCH_3}{\overset{\overset{4}{O}}{}}})_2 + (C_2H_5)_3SiI \xrightarrow{1,2} (C_2H_5)_3SiCH_2COOCH_3$$
$$\xrightarrow{1,4} CH_2=C(OSi(C_2H_5)_3)(OCH_3)$$

This dual reactivity of α-metallated carbonyl compounds was used by us to obtain isomeric C- and O-organoelement derivatives. Such pairs of isomeric compounds are of special interest since, depending on the relative stability of isomers, one can expect either the rearrangement of the thermodynamically less stable to the more stable isomer, or the establishment of a dynamic equilibrium between the isomers, i.e. elementotropy.

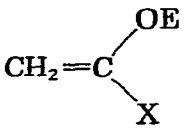
A feature of the majority of the studied reactions of the compounds possessing dual reactivity consists of the higher rate of formation of the O-derivatites (kinetic control), which turn out to be thermodynamically less stable than the C-isomers. Thus, the reaction between silicon tetrachloride and an ester of trialkylstannylacetic acid at low temperature proceeds with transter of the reaction centre and the formation of *O*-methyl-*O*-trichlorosilylketene acetal (kinetic control). This compound isomerizer even at room temperature and rapidly on gentle heating (70°, 30 min) to give the methyl ester of trichlorosilylacetic acid. This unique rearrangement, involving the breaking of an O—Si bond and formation of a new Si—C bond, is associated with the higher thermodynamic stability of the ester of trichlorosilylacetic acid [46]. Trialkylsilylacetone also undergoes isomerisation on heating, giving isopropenyloxytrialkylsilane:

$$R_3SiCH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow R_3SiO\underset{\underset{CH_3}{|}}{C}=CH_2$$

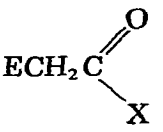
In this case a Si—C bond is broken and a new Si—O bond is formed, and this rearrangement can be regarded to some extent as the reverse of that considered above.

Subsequent studies of various isomeric pairs of O- and C-elemento-substituted carbonyl compounds have shown that the nature of the migrating group has a considerable effect on the stability of these forms and on the direction of the rearrangement. Thus, progressive attachment of chlorine atoms, having

a strong —*I*-effect, to silicon in place of alkyl groups manifesting +*I*-effects hinders rearrangement. A strong effect is exerted on the direction of the rearrangement and the stability of the O-isomer (I) or C-isomer (II) by the electronic effects of the substituent X attached to the central atom of the keto-enolic triad.

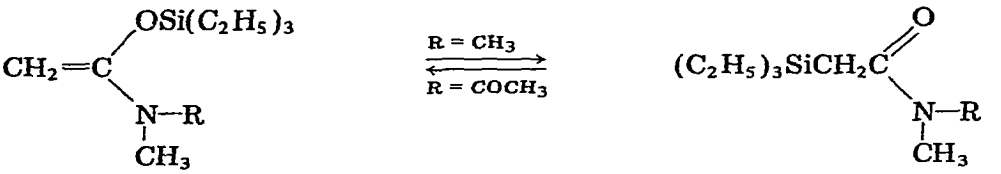


(I) O-isomer

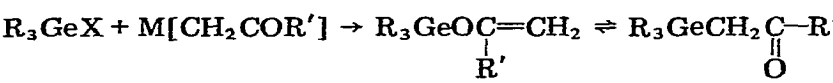


(II) C-isomer

The influence of these factors, and especially of the mesomeric effect, was conveniently studied by use of nitrogen analogues of trialkylsilylketene acetals and the isomeric substituted amides of trialkylsilylacetic acid. The results showed that an increase in the +*M*-effect of the substituent X facilitates the rearrangement of O-isomer into the C-derivative and increases the relative stability of the latter. In contrast, a decrease in the +*M*-effect or introduction of a substituent X having a —*M*-effect increases the relative stability of the O-isomer and facilitates the rearrangement of the C-isomer into the O-derivative. This is clearly demonstrated by the following example [47]:



These isomeric transformations of silicon-containing derivatives of the enolizing monocarbonyl compounds are irreversible. In investigating organoelement derivatives of keto-enols we discovered reversible tautomeric elementotropic interconversions. Thus, the interaction of metallo (Hg, Sn) derivatives of acetaldehyde, acetone and acetophenone with halides, hydrides, thiols and sulphides of germanium results in the initial formation of enolates of trialkylgermanium (kinetic control).



(R = CH_3, C_2H_5; M = Alk_3Sn, $HgCH_2COR'$; R′ = CH_3, C_6H_5; X = H, SH, ½S, Cl, Br)

The latter undergo gradual isomerisation to the C-derivative in the reaction mixture until the equilibrium state is attained (thermodynamic control). The rate of such an isomerisation depends on the reaction conditions and the presence of substances (e.g. halogermanes) capable of accelerating the attainment of equilibrium. In particular, with hydrides, thiols and sulphides of germanium as the starting materials the composition of the products is close to that corresponding to kinetic control, while with halogermanes the percentage of the C-isomer is larger and the ratio of isomers in the reaction mixture approaches the equilib-

rium ratio. The same effect results from use of more vigorous experimental conditions.

The pure O-isomer was obtained by the interaction between dimethylamino-

$$(C_2H_5)_3GeN(CH_3)_2 + CH_2{=}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{-}OCOCF_3 \rightarrow (C_2H_5)_3GeO\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}{=}CH_2 + CF_3CON(CH_3)_2$$

triethylgermane and isopropenyltrifluoroacetate [48]. In the case of trimethylgermylacetone, slow fractional distillation of the equilibrium mixture of isomers (containing 3% of the O-isomer at 20°) also gave the practically pure O-isomer, which gradually isomerized on standing until equilibrium was reached. With an increase in temperature the content of O-isomer in the mixture increases, and at 160° it reaches 12.5% [49].

The thermodynamic parameters of germanotropic equilibrium have been determined for certain pairs of isomers (see Table 1).

$$RC(OGeMe_3){=}CH_2 \rightleftharpoons Me_3GeCH_2\underset{\displaystyle O}{\overset{\displaystyle ||}{C}}R$$

In the case of the acetophenone derivatives, the constants for the germanotropic equilibrium correlated closely with the Hammett σ constants of the substituents, with $\rho = 1.67$. Therefore, for the germanotropic equilibrium (as for the keto-enol equilibrium) electron-donating substituents in the aromatic ring decrease and electron-accepting substituents increase the proportion of the O-isomers [50]. Thus, a dynamic germanotropic equilibrium between the O- and C-isomers ("slow tautomerism") is observed with germanium-constaining derivatives of enolizing monocarbonyl compounds.

An example of "rapid" tautomerism is observed with the organotin derivatives of acetaldehyde, acetone and acetophenone formed by interaction of trialkylmethoxystannanes with appropriate enol-acetates:

$$R_3SnOCH_3 + CH_2{=}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}OCOCH_3 \rightarrow \begin{cases} R_3SnCH_2\underset{\displaystyle O}{\overset{\displaystyle ||}{C}}{-}R' + CH_3COOCH_3 \\ R_3SnO{-}\underset{\displaystyle R'}{\overset{\displaystyle |}{C}}{=}CH_2 + CH_3COOCH_3 \end{cases}$$

The PMR data indicate that there is rapid intermolecular exchange of the or-

TABLE I

THERMODYNAMIC PARAMETERS OF GERMANOTROPIC EQUILIBRIUM PAIRS OF ISOMERS OF $RC(OGeMe_3){=}CH_2$

R	O-isomer (%) (20°)	C-isomer (%) (20°)	H_1 (kcal mol^{-1})	S (kcal mol^{-1} deg.$^{-1}$)
CH_3	3	97	2.64 ± 0.05	2.1 ± 0.1
p-$CH_3C_6H_4$	10.2	89.8	1.67 ± 0.15	1.33 ± 0.12
C_6H_5	17.1	82.9	1.35 ± 0.01	1.5 ± 0.2
p-ClC_6H_4	33.7	66.3	0.74 ± 0.05	1.19 ± 0.08

ganotin moiety between the derivatives of different ketones and a very rapid exchange between the O- and C-organotin isomers in the presence of trialkylhalostannanes. In the latter case, with a sufficient concentration of halostannane the rate of exchange is so fast that separate signals cannot even be observed in the NMR spectra, only the averaged signals of the O- and C-isomers (average life-time of molecule is 10^{-1}-10^{-3} sec) being seen [51].

The influence of the electronic effect of the substituent directly bonded to the carbonyl group has been already considered earlier. At the same time, for a certain class of compounds, e.g. ketones, steric factors can also play a significant role. The steric hindrance produced by the substituents on the α-carbon atom or on the element is greater for the C-isomer than for the O-isomer:

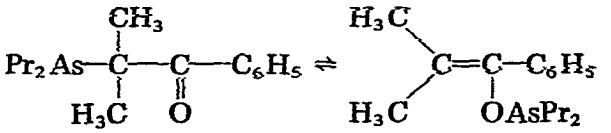
Thus, when the organoelement derivatives of the substituted carbonyl compounds have the C-structure, we can expect that an increase in steric hindrance will destabilize the C-form to a greater extent than the O-form, and the concentration of the latter in the tautomeric mixture will increase until it reaches a level which can be detected spectroscopically. In fact, in the case of organoantimony ketones the region of observable (IR, PMR) tautomeric equilibria involves derivatives of the ketones with a secondary carbon atom (cyclopentanone, cyclohexanone), while the derivatives of the ketones with a primary carbon atom ($\rangle SbCH_2\overset{\overset{O}{\|}}{C}R$) give only C-isomers, and those with a terriary carbon atom (isobutyrophenone) give only O-isomers [52-53].

Arsenic has a greater tendency than antimony to form the C-derivatives of carbonyl compounds, so that dipropyl- (or diphenyl)-arsylisobutyraldehyde (and cyclohexanone) are C-isomers. The presence of t-butyl groups on the arsenic atom leads to an O-structure for the compound. The O-di-t-butylarsenyl derivative of acetophenone rearranges almost completely into the C-isomer:

$$C_6H_5\overset{\overset{CH_2}{\|}}{C}-OAs\text{-}t\text{-}Bu_2 \rightarrow C_6H_5\overset{\overset{O}{\|}}{C}CH_2As\text{-}t\text{-}Bu_2$$

but in the case of the derivatives of propiophenone and isobutyrophenone such a rearrangement is not observed, and the O-form turns out to be the more stable.

By reducing the steric hindrance at the arsenic atom (by using i-Pr_2As and n-Pr_2As instead of t-Bu_2As groups) it is possible to observe the tautomeric equilibrium for the isobutyrophenone derivatives:



Univalent gold has the d^{10} configuration, therefore, the electronic d-sublevel is filled and the organic compounds of gold of the RAuZ type turn out to

be isostructural and isoelectronic with organomercury derivatives RHgX. The study of the reactions of the Au—C σ-bond conducted by me and my colleagues [54] has shown that the organogold compounds $RAuPR_3$ are rather close in some properties to the corresponding organomercury derivatives, R_2Hg and RHgX. An analogy was also discovered between the reactions of α-mercurated and α-aurirated carbonyl compounds MCH_2COR, where M = HgX or $AuPPh_3$, and R = hydrocarbon radical. Thus, triphenylphosphinegoldacetone reacts with the electrophilic reagents such as mercurated ketones with cleavage of the C—Au bond and formation of the corresponding C- or O-derivatives. The reactions at the C-atom involve acids, mercuric chloride and bromine. At the oxygen atom, the reaction takes place with acyl halides

$$CH_3—O—CH_2AuPPh_3 \xrightarrow{HCl} CH_3COCH_3 + ClAuPPh_3$$
$$\xrightarrow{HgCl_2} CH_3COCH_2HgCl + ClAuPPh_3$$
$$\xrightarrow{Br_2} CH_3COCH_2Br + BrAuPPh_3$$
$$\downarrow CH_3COCl$$
$$CH_2=C(CH_3)—OCOCH_3 + ClAuPPh_3$$

The α-aurated ketones were obtained by the direct auration of ketones (acetone, ethyl methyl ketone, acetophenone and acetylacetone) with the mixture of Ag_2O and $ClAuPPh_3$ or with tris(triphenylphosphinegold)oxonium salts [54-55].

$$R—C(=O)—CH_3 \xrightarrow[\text{or } [(Ph_3PAu)_3O]^+X^-]{Ag_2O + ClAuPPh_3} R—C(=O)—CH_2AuPPh_3$$

(R = CH_3, C_2H_5, C_6H_5)

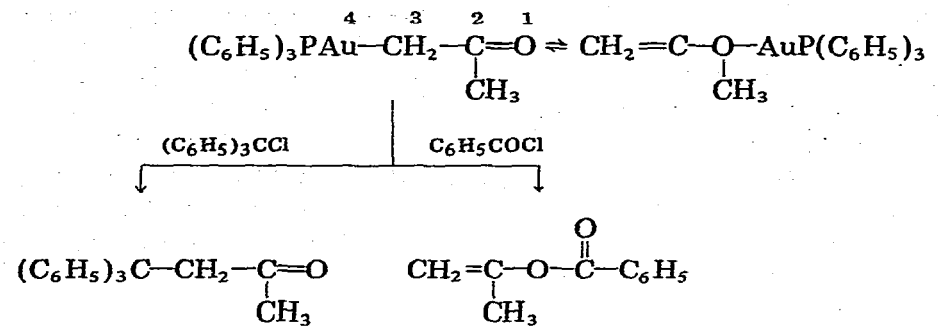
The aurated acetaldehyde is obtained from the reaction between vinyl n-butyl ether and tris(triphenylphosphinegold)oxonium tetrafluoroborate in an alkaline medium [55]:

$$CH_2=CHOC_4H_9 + [(PPh_3Au)_3O]^+BF_4^- \xrightarrow[THF/H_2O]{K_2CO_3} Ph_3PAuCH_2C(=O)H$$

Reactions of gold compounds with the ethers of enols and with carbonyl compounds were previously unknown.

Thus, the author and his coworkers have developed and used a large number of methods for obtaining organometallic compounds of mercury, boron, silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and lastly gold. In the case of organometallic derivatives of tautomeric prototropic systems, for a number of metals tautomeric organometallic compounds were obtained, and thus metallotropic tautomerism was discovered. It will be clear from our earlier publications [56-59], that as with prototropic tautomers, the dual reactivity of metallotropic tautomers is in general not connected with interconversion of the tautomers themselves. The dual reactivity can be intrinsic to each of the interconvertible forms of tautomers, as represented in the following scheme referring to the dual reactivity of $(C_6H_5)_3PAuCH_2—C(CH_3)=O$, which can give the

ketone or the enol derivative:



For this situation to be realized it is not necessary for a tautomeric equilibrium to exist between the two forms. One of them on its own can react with some reagents to form enol derivatives and with other reagents to form ketone derivatives. This occurs, as I have more than once proved [56-59], as a result of σ,π-conjugation between Au—C and C=O bonds, which gives rise to the possibility of electrophilic attack not only at the CH_2 moiety linked to Au (as in the case of a trityl cation attack), but also at the carbonyl oxygen, as in the case of benzoylation. The proposed existence of σ,π-conjugation has been much criticized; and an account of the arguments is given in a special issue of Tetrahedron [60] but this discussion did not lead to a definite conclusion. To the purely chemical evidence [see 56-59] in favour of σ,π-conjugation I hope in the near future to add physical evidence [61] which has until now been lacking, but shortage of space does not allow an account of this to be given here.

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