O- AND C-ISOMERIC ORGANOELEMENT DERIVATIVES OF KETO-ENOL SYSTEMS: REARRANGEMENTS AND ELEMENTOTROPISM

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ABSTRACT

The synthesis and investigation of the chemical behaviour of α-metallated aldehydes, ketones, esters and amides of carbonic acids and the dual reactivity of these compounds are described. Some results in the studies of the thermal stability of *O*- and *C*-isomeric elemento-organic derivatives of keto-enol systems, the conditions of the rearrangement of *C*-isomers into *O*-derivatives and vice versa, as well as effects of migrating group nature or environment on the sense of rearrangement and the electronic effects of substituent 'X', connected to the central atom of the keto-enol triad are discussed. The differences between rearrangements effected by chemical reagents and those in thermal conditions are considered and a summary on elementotropic tautomeric equilibria is presented.
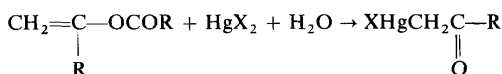
Among the various types of organometallic compounds, those containing a metal–carbon bond conjugated with a functional group were for a long time inaccessible. The exception was a series of mercurated alcohols belonging to a large group of organometallic derivatives which, owing to their chemical peculiarities, were termed quasi-complexes by Nesmeyanov.

Numerous attempts at working out unit methods of the synthesis of α-metallated carbonyl derivatives were, as a rule, unsuccessful. This was especially true for the organomercury derivatives. Such reactions as the direct mercuration by mercury salts, the action of mercuric oxide in alkaline media, oxidation of mercurated alcohols, and interaction of mercury salts with acetylene resulted in nothing but separate representatives of the required types[1].

An intensive study of the synthesis and chemical behaviour of α-metallated aldehydes, ketones, esters, and amides was started several years ago in Moscow University under the guidance of Nesmeyanov, the President of the Congress. In the course of these investigations, a unit procedure to obtain α-mercurated aldehydes and ketones was found, namely, the addition of mercury salts to enol ethers or enol esters[2].
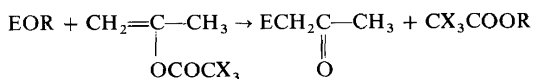
$$CH_2\!\!=\!\!\underset{\underset{R}{|}}{C}\!\!-\!OR' + HgX_2 + H_2O \rightarrow XHgCH_2\underset{\underset{O}{\|}}{C}\!\!-\!R$$

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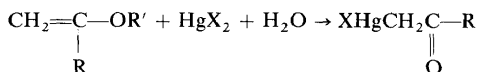
$$CH_2=C-OCOR + HgX_2 + H_2O \rightarrow XHgCH_2C-R$$
$$\underset{R}{|} \qquad\qquad\qquad\qquad \underset{O}{\|}$$

Enol esters were also shown to be applicable to the synthesis of derivatives of other metals[3].

$$R_3SnOCH_3 + CH_2=C-CH_3 \rightarrow R_3SnCH_2C-CH_3 + CH_3COOCH_3$$
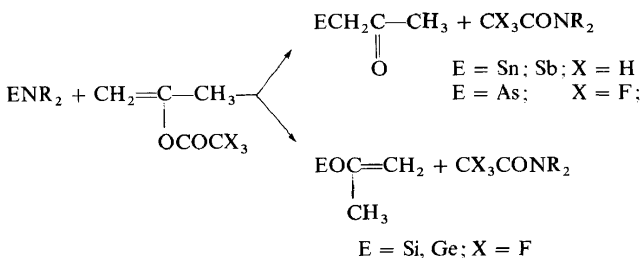$$\underset{OCOCH_3}{|} \qquad\qquad \underset{O}{\|}$$
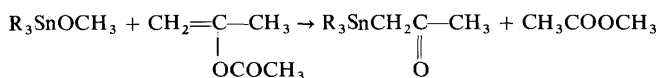
Further, it was shown that this reaction could be made much more versatile by varying the nucleophilicity and the electrophilicity of the substrate and the agent, respectively, as shown in the scheme[4] below.
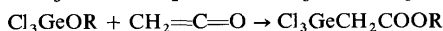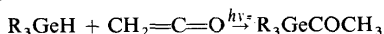
$$EOR + CH_2=C-CH_3 \rightarrow ECH_2C-CH_3 + CX_3COOR$$
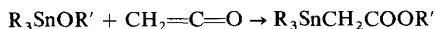$$\underset{OCOCX_3}{|} \qquad\qquad \underset{O}{\|}$$

E = Sn, X = H;
E = Sb, X = F;
E = Ge, X = F;

$$ECH_2C-CH_3 + CX_3CONR_2$$
$$\underset{O}{\|}$$

E = Sn; Sb; X = H
E = As;   X = F;

$$ENR_2 + CH_2=C-CH_3-\bigg\langle$$
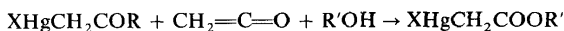$$\underset{OCOCX_3}{|}$$

$$EOC=CH_2 + CX_3CONR_2$$
$$\underset{CH_3}{|}$$

E = Si, Ge; X = F

Thus, enol esters are convenient compounds for obtaining functionally substituted organometallic compounds.

Another source of α-metallated carboxylic acids was the ketenes and their derivatives[5-7].

$$HgX_2 + CH_2=C=O + ROH \rightarrow Hg(CH_2COOR)_2$$

$$Hg(CH_2COR)_2 + CH_2=C=O \xrightarrow{\begin{array}{l}R'OH\\H_2O\\C_6H_6\end{array}} \begin{array}{l}Hg(CH_2COOR')_2\\Hg(CH_2COOH)_2\\Hg(CH_2COOC=CH_2)_2\\\qquad\qquad\quad |\\\qquad\qquad\quad R\end{array}$$

$$XHgCH_2COR + CH_2=C=O + R'OH \rightarrow XHgCH_2COOR'$$
$$R_3SnOR' + CH_2=C=O \rightarrow R_3SnCH_2COOR'$$
$$R_3GeH + CH_2=C=O \xrightarrow{h\nu} R_3GeCOCH_3$$
$$Cl_3GeOR + CH_2=C=O \rightarrow Cl_3GeCH_2COOR$$
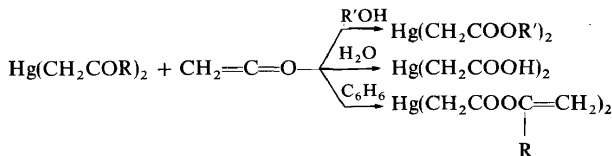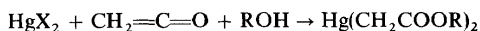
Alkoxygermanes can add to alkoxyacetylenes as well, producing the germylated acetals of ketene.

$$X_3GeOCH_3 + HC\!\!\equiv\!\!COR \rightarrow X_3GeCH\!\!=\!\!C\!\!\begin{array}{c} \diagup OR \\ \diagdown OCH_3 \end{array}$$
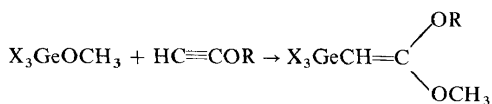
The syntheses of α-metallated aldehydes, ketones, and carboxylic acid derivatives which were discovered by us made the compounds quite accessible. Starting from these, we worked out methods to transfer functional groups from one organoelement compound to another through the action of organoelement halides, hydrides, sulphides, etc. This is partly reflected in the scheme below*.

$$R_3EH + Hg(CH_2CHO)_2\!\!-\!\!\begin{array}{c} \diagup R_3EOCH\!\!=\!\!CH_2 \quad (E = Si) \\ \diagdown R_3EOCH\!\!=\!\!CH_2 + R_3ECH_2CHO \ (E = Ge) \end{array}$$

$$R_3SiX + R'_nECH_2COR'' \rightarrow R_3SiOC\!\!=\!\!CH_2 \ (80\text{--}85\%, E = Hg, Sn. Ge)$$
$$\qquad\qquad\qquad\qquad\qquad\quad | \atop R''$$

$$R_3GeI + R'_nECH_2COR'' \rightarrow R_3GeCH_2COR'' \ (70\text{--}90\%, E = Hg, Sn)$$

$$R_3GeI + R'_nECH_2COOR'' \rightarrow R_3GeCH_2COOR'' \ (85\%, E = Hg, Sn)$$

$$GeCl_4 + nR_3SnCH_2COOCH_3 \rightarrow Cl_{4-n}Ge(CH_2COOCH_3)_n \ (75\text{--}90\%)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad n = 1\text{--}4$$

$$(R_3Si)_2S + Hg(CH_2COOR)_2 \rightarrow 2R_3SiCH_2COOR + HgS$$
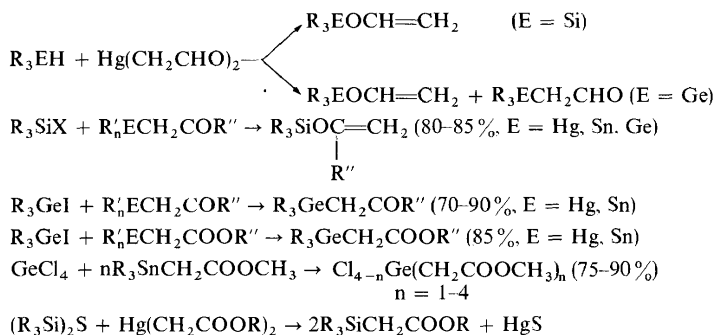
In this way, the number of functionally substituted organoelement compounds was extended considerably while novel organic derivatives of phosphorus, arsenic, antimony, and of other elements were synthesized. Of course, these reactions are important from the synthetical point of view. Their most promising feature, however, is that they clearly demonstrate the effect of conjugation of bonds upon the dual reactivity, the reaction site transfer, and upon rearrangements. When studying these processes, we found examples where the reaction could be directed at will towards the formation of either *C*- or *O*-organoelement derivatives which, in turn, could be subjected to a reversible or irreversible isomerization.

It is noteworthy that although functionally substituted organoelement compounds were dealt with in a great number of papers, the relative stabilities of the *C*- and *O*-derivatives of keto-enol systems were rarely reported. For example, the reaction of derivatives of the Group IVB elements with enolizable carbonyl compounds was, as a rule, reported to give just one of the products while the formation or isolation of the two isomers was only occasionally reported. The latter cases are especially interesting since the respective reactions may be expected to result either, in a rearrangement of the thermodynamically unstable isomer to the stable one, or in the equilibration of the isomers, in other words, the elementotropism.

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* cf. the reviews[8, 9] and the references cited therein.

α-Metallated aldehydes, ketones, or esters display two peculiarities. Their reactivity is unusually high compared to that of the alkyl and aryl derivatives and, on the other hand, they possess a clearly pronounced dual reactivity which is not accompanied by any tautomerism, viz., not by that of the initial compounds[10].
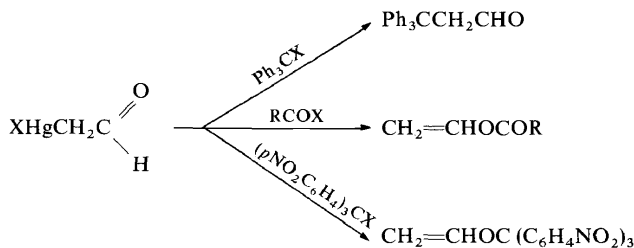
In the first reaction, the substituent takes the place of the metal; the second and third processes proceed via the reaction site transfer (as termed by Nesmeyanov) and result only in the vinyl esters. For the triarylhalomethanes, the change in electrophilicity leads to a change in the direction of the attack, as shown in the above scheme.

The reaction is affected by various factors such as the nature of the metal, the structure of the organometallic compound, and the nature of the agent, as well as the nature of the solvent. The reaction may be directed towards the formation of the desired product by merely changing the solvent. For example, diphenylphosphine reacts with mercury-bisacetone in various solvents to give the products shown in the Table[11].
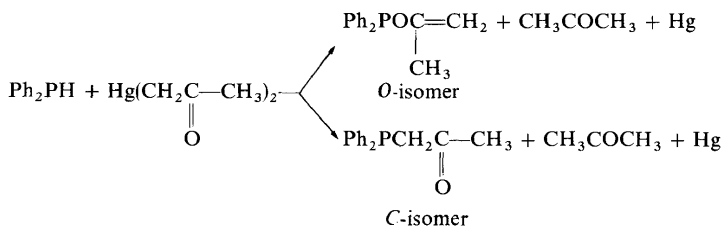
| Solvent | Isomer content, per cent | |
	O-isomer	C-isomer
Benzene	none	100
Chlorobenzene	none	100
Dioxane	30	70
Monoglyme	70	30

The percentage was found by integrating the ¹H n.m.r. signals and the isomers were separated by vacuum distillation. The Table demonstrates that the greater the basicity and the coordinating ability of the solvent, the more

active are the reaction site transfer and the formation of the *O*-species, *O*-isopropenyl diphenylphosphinite.

Similarly, the dual reactivity was observed for the reaction of α-metallated carboxylic esters with halo- or organohalosilanes[12].
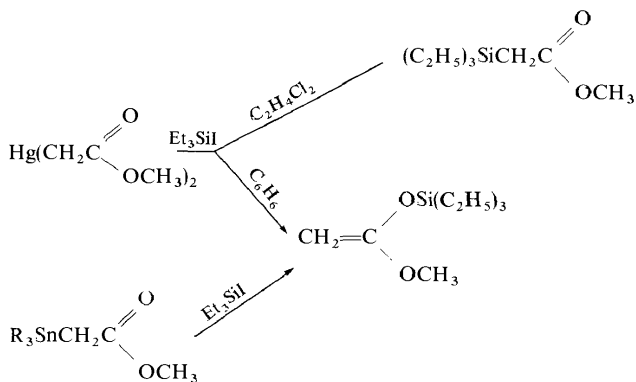
Further, it was shown that halosilanes reacted with the metallated acetic esters via two successive steps, namely,

(i) The *O*-silylation product was formed (the reaction site transfer, kinetic control);

(ii) A unique rearrangement occurred which consisted of O—Si bond fission and Si—C bond formation (thermodynamic control).

For instance, when silicon tetrachloride is mixed with methyltrialkyl-stannyl acetate and the mixture cooled, *O*-methyl-*O*-trichlorosilylketene acetal is formed. At room temperature the product isomerizes (the isomerization takes 30 min at 70°C) to methyl trichlorosilyl acetate.
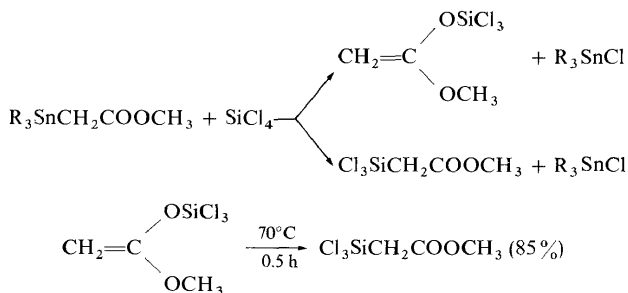
Such transformations may be easily observed by i.r. spectroscopy since the bands of the individual components are not superimposed. Trichloromethylsilane or dimethylsilyl dichloride react with stannylated acetic esters analogously and give the *O*-silylation product under mild conditions, and the *C*-derivatives under more drastic conditions.

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Conditions	SiCl$_3$	MeSiCl$_2$	Me$_2$SiCl	Et$_3$Si
Temperature, °C	70	90	90	200
Duration, h	0.5	5	9	decomposes

We found that most of the compounds apt to the dual reactivity were characteristic in that the O-isomers were formed at noticeably high rates (kinetic control) while they turned out to be less thermodynamically stable than the C-isomers. When the chlorines attached to the silicon and characterized by a strong $-I$ effect are successively replaced by alkyls, characterized by a $+I$ effect, the thermal rearrangement is significantly hindered. When trichlorosilyl is replaced by trialkylsilyl, the rearrangement rate becomes practically zero.

In going from silicon to germanium and tin, the stability of the C-isomers increases. For example, alkoxystannanes react with ketene to produce only the metallated acetic esters[1, 13].

$$R_3SnOR' + CH_2{=}C{=}O \rightarrow R_3SnCH_2COOR'$$
$$R_2Sn(OR')_2 + 2CH_2{=}C{=}O \rightarrow R_2Sn(CH_2COOR')_2$$
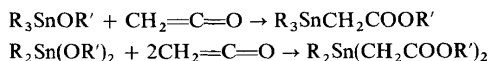
Stannylated acetic esters react with halo- or organohalogermanes to give the C-derivatives[7] only. We found a number of reactions which indicate that O-germyl-O-alkylketene-acetals were formed initially, followed by the isomerization to the germylated acetic esters.
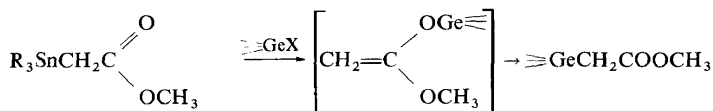
Thus, the C- and O-form stability, as well as the rearrangement direction, are greatly affected by the nature of the migrating group and by the substituents attached to the element. When the Pauling electronegativity of the element decreases, and when the $-I$ groups bonded to it are replaced by the $+I$ groups, the O-isomer stability rises while the rearrangement to the C-species slows down. With silicon, the increase in the O-isomer stability may be due to the additional p_π–d_π bonding which decreases significantly when silicon is replaced by germanium or tin.
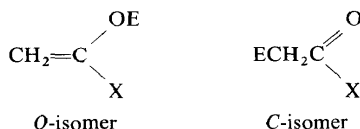
O-isomer C-isomer

A powerful influence upon the rearrangement direction and the O- or C-isomeric stability is displayed by electronic effects of the substituent X bonded to the central atom of the keto-enol triad. The system turned out to

be extremely sensitive to even slight variations in the electronic nature of the substituent, which affected not only the thermal stability of the isomers but also the rearrangement direction.

The influence of these factors, especially of the mesomeric effect, can be readily observed with nitrogen-containing analogues of silylated ketene ace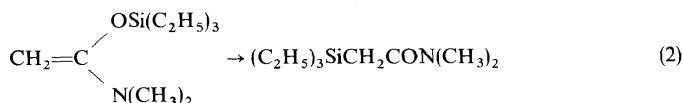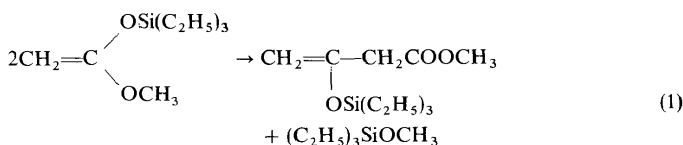tals[14]. If ketene is allowed to react with silylated dimethylamine at $-10°$ to $-15°C$, a nitrogen-containing analogue of the silylated ketene acetal will be formed.
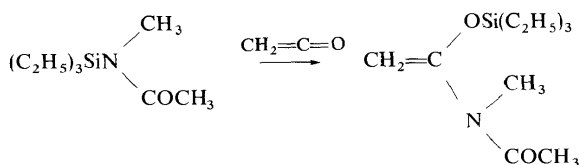
$$(C_2H_5)_3SiN(CH_3)_2 \xrightarrow{\quad CH_2=C=O \quad} CH_2=C \begin{smallmatrix} OSi(C_2H_5)_3 \\ \\ N(CH_3)_2 \end{smallmatrix}$$
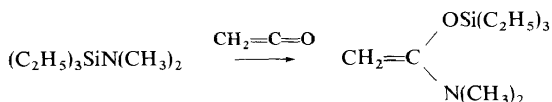
O-Triethylsilyl-O-methylketene acetal, when heated to 180–200°C, yields no C-isomer but decomposes according to equation 1

$$2CH_2=C\begin{smallmatrix} OSi(C_2H_5)_3 \\ \\ OCH_3 \end{smallmatrix} \rightarrow CH_2=C-CH_2COOCH_3 \begin{smallmatrix} | \\ OSi(C_2H_5)_3 \end{smallmatrix} \\ + (C_2H_5)_3SiOCH_3 \qquad (1)$$

$$CH_2=C\begin{smallmatrix} OSi(C_2H_5)_3 \\ \\ N(CH_3)_2 \end{smallmatrix} \rightarrow (C_2H_5)_3SiCH_2CON(CH_3)_2 \qquad (2)$$

whereas the nitrogen-containing analogue rearranges in several days at room temperature, or much more rapidly at 140°C, (2). These data show that an increase in the $+M$ effect of the substituent facilitates the rearrangement and raises the relative stability of the C-isomer.

When one of the methyl groups in the silylated amine is replaced by an acetyl group, the reaction with ketene is not hindered.

$$(C_2H_5)_3SiN\begin{smallmatrix} CH_3 \\ \\ COCH_3 \end{smallmatrix} \xrightarrow{\quad CH_2=C=O \quad} CH_2=C\begin{smallmatrix} OSi(C_2H_5)_3 \\ \\ N \begin{smallmatrix} CH_3 \\ \\ COCH_3 \end{smallmatrix} \end{smallmatrix}$$

However, when an electron-accepting group is attached to the nitrogen, the compound obtained from the reaction with ketene cannot undergo the thermal rearrangement which would result in the C-species. Furthermore, the C-derivatives synthesized via an independent route

$$(C_2H_5)_3SiCH_2COOH \xrightarrow{\quad PCl_3 \quad} (C_2H_5)_3SiCH_2COCl \longrightarrow$$

$$\xrightarrow{\quad (CH_3)_3SiN\begin{smallmatrix} CH_3 \\ \\ COCH_3 \end{smallmatrix} \quad} (C_2H_5)_3SiCH_2C\begin{smallmatrix} O \\ \parallel \\ \end{smallmatrix}-N\begin{smallmatrix} CH_3 \\ \\ COCH_3 \end{smallmatrix}$$

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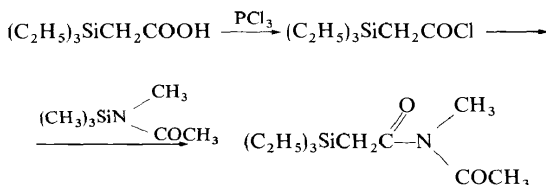
completely isomerize to the *O*-derivatives on heating. Thus, when the methyl group is replaced by an acetyl group in the *C*-silylated acetic acid amides, the direction of isomerization is reversed.

$$CH_2=C\begin{array}{c} OSi(C_2H_5)_3 \\ CH_3 \\ N-CH_3 \end{array} \rightarrow (C_2H_5)_3SiCH_2C\begin{array}{c} O \\ CH_3 \\ N-CH_3 \end{array}$$

$$(C_2H_5)_3SiCH_2-C\begin{array}{c} O \\ CH_3 \\ N-COCH_3 \end{array} \rightarrow CH_2=C\begin{array}{c} OSi(C_2H_5)_3 \\ CH_3 \\ N-COCH_3 \end{array}$$

$$CH_2=C\begin{array}{c} OSi(C_2H_5)_3 \\ CH_3 \\ N-A \end{array} \underset{A=COCH_3}{\overset{A=CH_3}{\rightleftharpoons}} (C_2H_5)_3SiCH_2C\begin{array}{c} O \\ CH_3 \\ N-A \end{array}$$
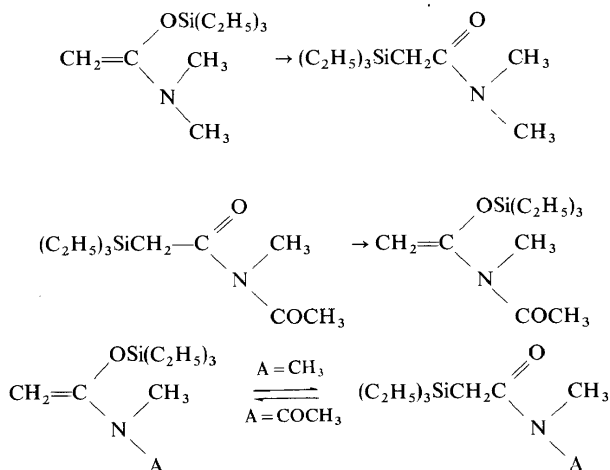
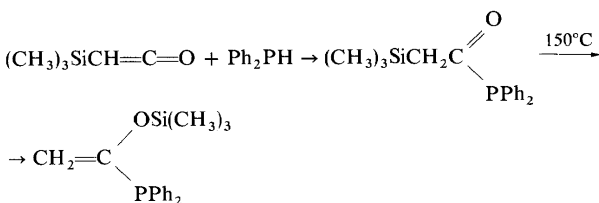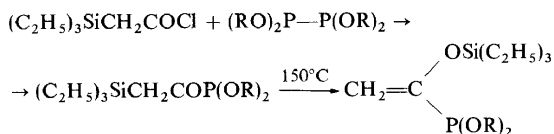These data demonstrate that a decrease in the $+M$ effect raises the relative stability of the *O*-isomer and favours the *C*- to *O*-rearrangement. This will be even more apparent for a $-M$ group playing the part of the substituent X.

From the results discussed above, we could predict and accomplish a number of novel isomerizations. To begin with, we studied thermal stability of the compounds whose substituent X was a three or four-coordinated phosphorus. A three-coordinated phosphorus is known to be an acceptor which is, however, much weaker than the strong electron-accepting phosphoryl group. First the addition of diphenylphosphine to trimethylsilyl-ketene was studied. The reaction results in the *C*-structured product.

$$(CH_3)_3SiCH=C=O + Ph_2PH \rightarrow (CH_3)_3SiCH_2C\begin{array}{c} O \\ PPh_2 \end{array} \xrightarrow{150°C}$$

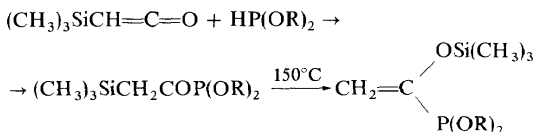$$\rightarrow CH_2=C\begin{array}{c} OSi(CH_3)_3 \\ PPh_2 \end{array}$$

which rearranges irreversibly to the *O*-derivative on heating at as high a temperature as 140–150°C: β-(triethylsilyl)acetylphosphonite behaves similarly.

$$(C_2H_5)_3SiCH_2COCl + (RO)_2P-P(OR)_2 \rightarrow$$

$$\rightarrow (C_2H_5)_3SiCH_2COP(OR)_2 \xrightarrow{150°C} CH_2=C\begin{array}{c} OSi(C_2H_5)_3 \\ P(OR)_2 \end{array}$$

The analogous C-derivatives obtained by the addition of dialkoxyphosphine to trimethylsilylketene rapidly rearranges into the O-species on heating. Under usual temperatures the rearrangement is complete after a week.
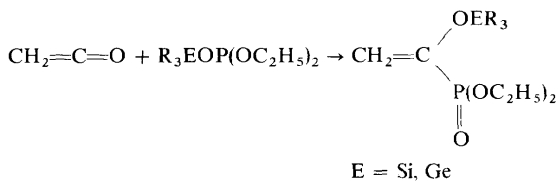
$$(CH_3)_3SiCH=C=O + HP(OR)_2 \rightarrow$$

$$\rightarrow (CH_3)_3SiCH_2COP(OR)_2 \xrightarrow{150°C} CH_2=C\begin{array}{l} {}^{OSi(CH_3)_3} \\ {}_{P(OR)_2} \end{array}$$

The reaction series below was aimed at obtaining the C-isomer which would contain a four-coordinated phosphorus as the substituent X[15].
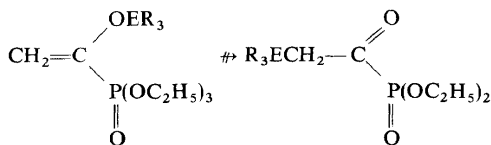

E = Si. Ge.
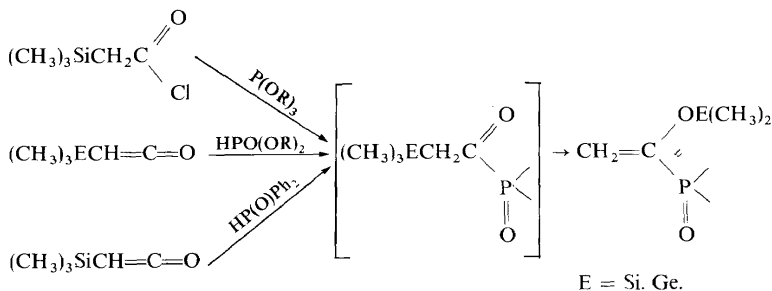
The spectra have never revealed the presence of the C-isomers although only this isomer should have been formed in the reaction. Instead, the O-isomer was isolated in all cases. Consequently, when the substituent X is such a strong electron acceptor as the phosphoryl group, the C-isomer rapidly rearranges to the O-species even at room temperature. The difference between the electron-accepting properties of the three and four-coordinated phosphorus atoms leads to the different thermal stabilities of the C-isomers formed. The effect of the electron-accepting substituent X on the relative stability of the C- and O-isomers, discussed above, leads one to expect that in these cases the more stable species, the O-isomer will be formed. This turns out to be perfectly true. The process is facilitated by the strong electron-accepting phosphoryl group.

These conclusions agree with the other series of reactions studied by us, namely, the addition of silyl or germyl phosphites to ketene[16].
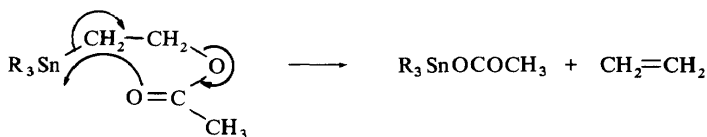
$$CH_2=C=O + R_3EOP(OC_2H_5)_2 \rightarrow CH_2=C\begin{array}{l} {}^{OER_3} \\ {}_{\underset{\parallel}{P(OC_2H_5)_2}} \\ {}_{O} \end{array}$$

E = Si, Ge

The O-derivatives were inevitably obtained. They did not rearrange to the C-isomers.

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$$CH_2=C \overset{OER_3}{\underset{\underset{O}{\overset{||}{P(OC_2H_5)_3}}}{\diagdown}} \nrightarrow R_3ECH_2-C \overset{O}{\underset{\underset{O}{\overset{||}{P(OC_2H_5)_2}}}{\diagup}}$$

This demonstrates once more that the stability of the O- and C-isomers, and hence the isomerization direction, is governed by the nature of the substituent X.

We have discussed the thermal stability of element-substituted O- and C-isomeric keto-enol derivatives as a function of the nature of the element E, the groups attached thereto, and of the nature of the substituent X bonded to the central atom of the keto-enol triad. The results predict that, apart from the rearrangements mentioned above, a number of similar rearrangements exist which obey the same qualitative regularities.

In 1966 Musker showed spectroscopically that the silicon in α-silylated ketones could coordinate to the carbonyl group intramolecularly[17]. In a study of organotin compounds containing a functional group in the organic moiety, we found a similar coordination in β-acetoxyethyl trialkylstannanes. The coordination may facilitate the thermal decomposition of the compounds via a six-membered transition state.

$$R_3Sn \overset{\overset{CH_2-CH_2}{\diagup \diagdown}}{\underset{\underset{CH_3}{O=C \diagdown}}{\diagdown O}} \longrightarrow R_3SnOCOCH_3 + CH_2=CH_2$$
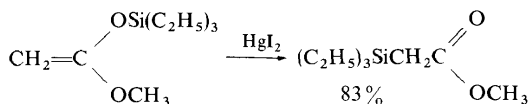
Our results concerning the relative stabilities of α-silylated ketones and the isomeric silylated enols agree with the above data. We showed that both types were sufficiently stable and were not isomerized under normal conditions. However, when heating them at 160–180°C for two to three hours, α-silylated ketones rearrange to the O-silylated enols[18].

$$R_3SiCH_2C \overset{||}{\underset{O}{}}-R' \rightarrow CH_2=C \overset{|}{\underset{OSiR_3}{}}-R'$$
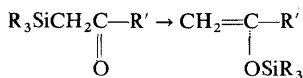
The thermal isomerization of triethylsilylacetone, mixed with trimethylsilylacetophenone, results in only two rearrangement products, triethylisopropenyloxysilane and trimethylstyryloxysilane. The isomerization may proceed intramolecularly via a four-membered transition state. Dr. Brook, who discovered the rearrangement simultaneously with us, came to similar conclusions[8, 19].

The rearrangements of the thermodynamically less stable isomers to the more stable ones can be induced not only thermally but also chemically (the action of mercuric iodide, iodosilanes, etc.). For instance, O-triethylsilyl-O-methylketene acetal, which does not rearrange on heating, produces

methyl triethylsilyl acetate when acted upon by mercuric iodide (several molar per cent) even at room temperature. At moderate heating, the rearrangement is faster.

$$CH_2{=}C\overset{\displaystyle OSi(C_2H_5)_3}{\underset{\displaystyle OCH_3}{\Big\langle}} \xrightarrow{HgI_2} (C_2H_5)_3SiCH_2C\overset{\displaystyle O}{\underset{\displaystyle OCH_3}{\Big\langle}}$$
$$83\%$$

With strong spontaneous heating in the presence of mercuric iodide or an iodosilane α-silylated ketones rearrange in several minutes.
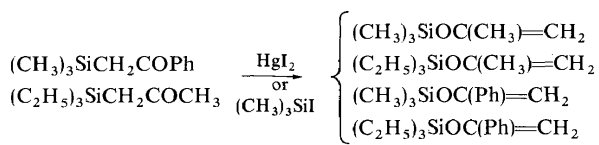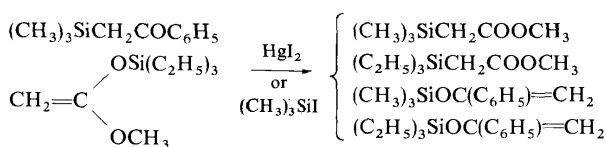
$$R_3SiCH_2COCH_3 \xrightarrow{HgI_2} CH_2{=}C{-}OSiR_3$$
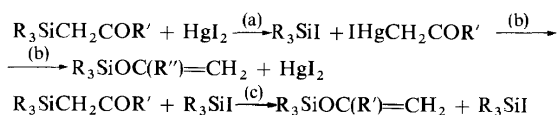$$\underset{\displaystyle CH_3}{\Big|}$$
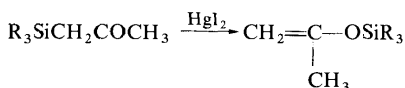
In this case, however, the rearrangement mechanism sharply differs from that of the thermal isomerization discussed above. For instance, unlike the thermal rearrangement, the action of mercuric iodide (or of trimethyliodosilane) on a mixture of triethylsilylacetone and trimethylsilylacetophenone results in four, instead of two, O-silylated enols.

$$\begin{array}{l} (CH_3)_3SiCH_2COPh \\ (C_2H_5)_3SiCH_2COCH_3 \end{array} \xrightarrow[\underset{(CH_3)_3SiI}{or}]{HgI_2} \left\{ \begin{array}{l} (CH_3)_3SiOC(CH_3){=}CH_2 \\ (C_2H_5)_3SiOC(CH_3){=}CH_2 \\ (CH_3)_3SiOC(Ph){=}CH_2 \\ (C_2H_5)_3SiOC(Ph){=}CH_2 \end{array} \right.$$

O-methyl-O-triethylsilylketene acetal isomerized together with the silylated ketone under the action of mercuric iodide also gave four compounds.

$$\begin{array}{l} (CH_3)_3SiCH_2COC_6H_5 \\ CH_2{=}C\overset{\displaystyle OSi(C_2H_5)_3}{\underset{\displaystyle OCH_3}{\Big\langle}} \end{array} \xrightarrow[\underset{(CH_3)_3SiI}{or}]{HgI_2} \left\{ \begin{array}{l} (CH_3)_3SiCH_2COOCH_3 \\ (C_2H_5)_3SiCH_2COOCH_3 \\ (CH_3)_3SiOC(C_6H_5){=}CH_2 \\ (C_2H_5)_3SiOC(C_6H_5){=}CH_2 \end{array} \right.$$

This indicates an intermolecular isomerization. We assume that the action of mercuric iodide starts with the formation of the halomercurated acetone and the trialkyliodosilane. The latter may undergo the reaction site transfer in its interaction with either the organomercurial or the initial silylated ketone. These processes lead to the final products.

$$R_3SiCH_2COR' + HgI_2 \xrightarrow{(a)} R_3SiI + IHgCH_2COR' \xrightarrow{(b)}$$
$$\xrightarrow{(b)} R_3SiOC(R''){=}CH_2 + HgI_2$$
$$R_3SiCH_2COR' + R_3SiI \xrightarrow{(c)} R_3SiOC(R'){=}CH_2 + R_3SiI$$

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The fact that the steps (b) and (c) do occur was verified through independent experiments. A similar scheme may be assumed for the isomerization of O-alkyl-O-silylketene acetals to their C-isomers. Thus, the most stable isomer is formed and the rearrangement is practically irreversible: its overall rate should be governed by the ratio of the rates characterizing each of the steps.

This point of view allows a better understanding of the results obtained for the reaction of the esters of mercury-bisacetic acid with iodosilanes. If the reaction is carried out so that only iodomercuryacetic esters are formed, then one can obtain either the O- or the C-isomer by varying the solvent[20]. At higher conversion (the formation of mercuric iodide), the C-derivative is formed in all cases, regardless of the solvent applied[21].

$$
\text{Hg(CH}_2\text{COOR)}_2 + \text{R}_3\text{SiI} \longrightarrow
\begin{array}{l}
\text{CH}_2{=}\text{C} \begin{array}{l} \diagup\text{OSiR}_3 + \text{IHgCH}_2\text{COOR} \\ \diagdown \\ \text{OR} \end{array} \\
\text{R}_3\text{SiCH}_2\text{COOR} + \text{IHgCH}_2\text{COOR}
\end{array}
$$

$$
\text{Hg(CH}_2\text{COOR)}_2 + 2\text{R}_3\text{SiI} \rightarrow 2\text{R}_3\text{SiCH}_2\text{COOR} + \text{HgI}_2
$$
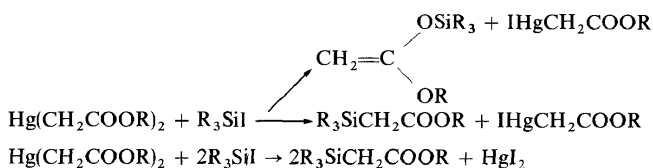
The same scheme may describe a novel rearrangement which we have recently found, viz. the isomerization of α,β-unsaturated phosphinites to the phosphines under the action of mercuric iodide, trialkyliodostannanes, cadmium iodide, etc.

$$
\text{R}_2\text{POC}{=}\text{CH}_2 \underset{\text{R}'}{\overset{\text{CdI}_2}{\longrightarrow}} \text{R}_2\text{PCH}_2\text{C}{-}\text{R}'
$$
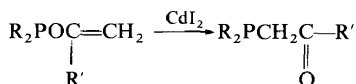
Unlike the well-known rearrangements the phosphorus does not change its valence, remaining trivalent. A similar rearrangement proceeds more easily in the case of some arsenous enolates. So dibutylstyroxyarsine is entirely rearranged into dibutylphenacylarsine even on distillation.

$$
\underset{\text{OAs(Bu}^t)_2}{\text{PhC}{=}\text{CH}_2} \rightarrow \text{PhCOCH}_2\text{As(Bu}^t)_2
$$
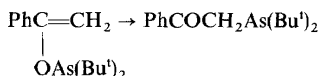
We hope to have demonstrated that our irreversible isomerizations proceed in the presence of various compounds under mild conditions. It should be always borne in mind that the products isolated from the reactions of compounds capable of displaying dual reactivity might sometimes differ from the products initially formed.

The isomerizations discussed above are characteristic in that they imply a practically irreversible transformation of thermodynamically less stable isomers to the more stable ones. Let us now consider reversible isomerizations. The boundary between the isomerization types is, of course, rather arbitrary since both the types are governed by the same factors, which have already been mentioned. Reversible isomerizations merit special attention

since they relate to a novel phenomenon, the tautomerism of metal-substituted keto-enol systems.

However vast, the literature concerned with tautomeric systems, with positions of tautomeric equilibria and factors governing these, and with mechanisms of the transformations, reactivity of the systems etc., deals, as a rule, with the prototropic rearrangements. In these cases, it was found that the compounds capable of displaying tautomeric transformations were, in the simplest cases, able to produce two isomeric series corresponding to the two tautomeric structures. In other words, they displayed dual reactivity (DR).

The close relation of tautomerism and DR led at that time to the conclusion that DR was not only the necessary but also the sufficient criterion for tautomerism. Consequently, tautomeric equilibria were postulated for all compounds which displayed DR, in particular, for metal-substituted keto-enol systems. Later, one more theory appeared which ascribed DR of metal-substituted keto-enol derivatives to the mesomerism of the β-dicarbonyl anions. This theory was related both with the absence of any experimental verification of the presumable tautomerism and with the fact that the enolate structures of the keto-enol derivatives were proved unambiguously.
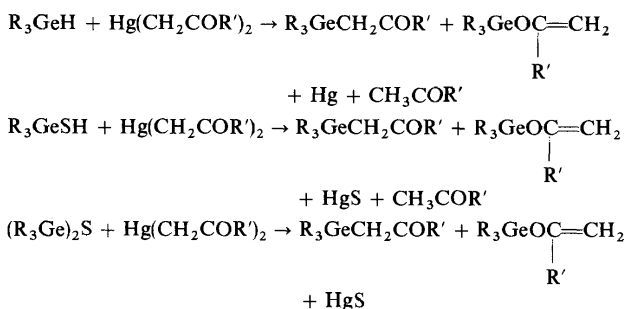
Another approach was worked out by Nesmeyanov about twenty years ago[22]. His work helped to discern between DR and tautomerism. It was shown that tautomerism was just a particular case of DR since the latter could be observed in the absence of any tautomeric equilibrium. For instance, metal-substituted derivatives of keto-enol systems were experimentally found to display the dual reactivity whether they were strictly C-structured (α-mercurated aldehydes and ketones) or strictly O-structured (lithium-, sodium-, or magnesium-substituted cis-trans-isomeric diphenyl-propiomesitylene enolates). Nesmeyanov assumed that the DR of the compounds was governed by their ability to undergo the reaction site transfer. Another important conclusion was that metal-substituted tautomeric systems could possess structures in which the bonds were localized, so the concept of the mesomeric anion was shown to be not necessarily valid. Further, at a sufficiently low difference between the energies of the isomers, one would expect that the metal-substituted derivatives would undergo a tautomeric transformation. Indeed, Nesmeyanov and Kravtsov found the first example of such a process, the tautomery of arylmetallated nitrosophenols[23].

Recently, tautomeric transformations, in particular non-prototropic ones, have become the subject of considerably more extensive work. Perhaps this may be explained by the fact that spectral methods, e.g. nuclear magnetic resonance techniques, may be used to study the systems whose interconversion rate is so high that the isomers cannot be isolated. Various non-
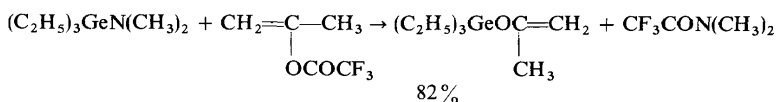
prototropic migrations have been reported, e.g. those of alkyl groups or metal cations in the alkyl cyclopentadienyls and related systems, or the migrations in fluxional systems. A new type of tautomery, valence tautomerism, has been discovered. However, there was no experimental verification of an equilibrium isomerization accompanied by the migration of an organoelement moiety or of a metal atom from one of the terminal atoms of a keto-enol system to the other atom, in other words, from O to C or vice versa. We have obtained these data by studying α-germylated carbonyl compounds and, later, the analogous organotin compounds.

The exchange reactions of metal-substituted (mercury, tin) derivatives of acetone or acetaldehyde with trialkylgermyl hydrides, thiols, sulphides, or halides have been shown to result in mixtures of two different germanium-containing products: an α-germylated carbonyl compound (C-isomer) and an O-germylated enol (O-isomer)[24].

$$R_3GeH + Hg(CH_2COR')_2 \rightarrow R_3GeCH_2COR' + R_3GeOC\!\!=\!\!CH_2$$
$$\underset{R'}{|}$$
$$+ Hg + CH_3COR'$$
$$R_3GeSH + Hg(CH_2COR')_2 \rightarrow R_3GeCH_2COR' + R_3GeOC\!\!=\!\!CH_2$$
$$\underset{R'}{|}$$
$$+ HgS + CH_3COR'$$
$$(R_3Ge)_2S + Hg(CH_2COR')_2 \rightarrow R_3GeCH_2COR' + R_3GeOC\!\!=\!\!CH_2$$
$$\underset{R'}{|}$$
$$+ HgS$$

Trialkylgermyl hydrides, thiols, or sulphides produce the O-isomer almost exclusively whereas the halides give the two isomers. The reaction of triethylgermyl bromide with mercury-bisacetone, traced by i.r. spectroscopy, reveals that the O-isomer is formed initially and is then isomerized to the C-derivative, the final reaction product. Thus, α-mercurated carbonyl compounds undergo the reaction site transfer when they react with the trialkylgermanium derivatives, and produce the O-germylated enols which, depending on the conditions, isomerize to the α-germylated carbonyl compounds more or less easily.
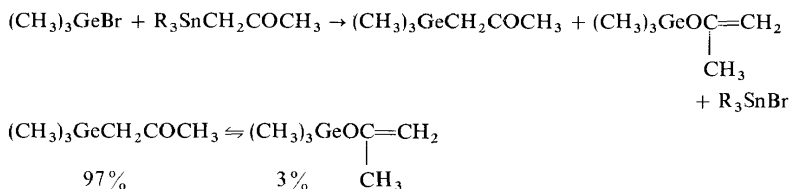
The pure O-isomer is obtained from the reaction of dimethylamino-triethylgermane with isopropenyl trifluoroacetate (10°C, 30 min)[4].

$$(C_2H_5)_3GeN(CH_3)_2 + CH_2\!\!=\!\!\underset{\underset{OCOCF_3}{|}}{C}\!\!-\!\!CH_3 \rightarrow (C_2H_5)_3GeOC\!\!=\!\!CH_2 + CF_3CON(CH_3)_2$$
$$\underset{\underset{82\%}{CH_3}}{|}$$

In this case, the O- to C-isomeric transformation is extremely slow: the compound measured by i.r. and ^{1}H n.m.r. spectroscopy 24 hours after it had been isolated displayed nothing but the absorption due to the O-isomer. The conversion is only 30 per cent after fourteen days. The transformation

becomes faster under more drastic experimental conditions, or in the presence of a halogermane.
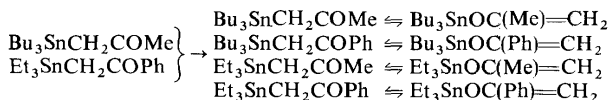
It should be emphasized that in all our isomerizations the *O-* to *C*-interconversions are never complete and the *O*-isomers are always present in the reaction mixtures. This may be explained by assuming a dynamic equilibration of the isomers. The equilibration rate, as measured qualitatively by us, for germanium derivatives, increases in going from the acetaldehyde derivatives to the acetone derivatives. It also increases with a decrease in the size of alkyls attached to the germanium.

$$(CH_3)_3GeBr + R_3SnCH_2COCH_3 \rightarrow (CH_3)_3GeCH_2COCH_3 + (CH_3)_3GeOC\!\!=\!\!CH_2$$
$$| $$
$$CH_3$$
$$+ R_3SnBr$$

$$(CH_3)_3GeCH_2COCH_3 \rightleftharpoons (CH_3)_3GeOC\!\!=\!\!CH_2$$
$$|$$
$$97\% \qquad\qquad 3\% \qquad CH_3$$

The trimethylisopropenyloxygermane–trimethylgermylacetone equilibrium has been studied in more detail. When distilling an almost equilibrated mixture of the isomers at normal pressure, the mixture is enriched in the *O*-isomer (60 per cent *O-*, 40 per cent *C*-derivative). Slow fractionation at a reduced pressure may yield the pure *O*-isomer, its amount greatly exceeding that in the mixture before fractionation. The *O*-species isomerizes, slowly in the absence of any admixture and rapidly in the presence of trimethylgermyl bromide, to produce the equilibrated mixture containing 3 per cent *O-* and 97° *C*-isomer. The equilibrium is temperature dependent; the *C*-isomer concentration increases with temperature and reaches *c.* 13 per cent at 160°C. On decreasing the temperature, the system returns to its initial state. Thus, the system displays a tautomeric germanotropic equilibrium of the enolate and the carbeniate species, which may be shifted to the left or to the right.

The germanotropism in keto-enols is an example of a slow tautomery. In this case, the interconversion is slow, and so the isomers are discernible on the n.m.r. time scale and may sometimes be isolated as the individual compounds.

The transformations of the analogous organotin compounds[25] are much faster. The high rate of migration of an organotin group from a keto-enol moiety to the other may be estimated by ^{1}H n.m.r. The spectrum has been recorded immediately after mixing two organotin derivatives of different ketones which contain different groups attached to the tin atoms. The spectrum reveals the presence of

$$\left.\begin{array}{l}\\ Bu_3SnCH_2COMe \\ Et_3SnCH_2COPh \end{array}\right\} \rightarrow \begin{array}{l} Bu_3SnCH_2COMe \rightleftharpoons Bu_3SnOC(Me)\!\!=\!\!CH_2 \\ Bu_3SnCH_2COPh \rightleftharpoons Bu_3SnOC(Ph)\!\!=\!\!CH_2 \\ Et_3SnCH_2COMe \rightleftharpoons Et_3SnOC(Me)\!\!=\!\!CH_2 \\ Et_3SnCH_2COPh \rightleftharpoons Et_3SnOC(Ph)\!\!=\!\!CH_2 \end{array}$$

the four *C*-derivatives. Nevertheless, although the exchange of the functional groups is fast enough, the ^{1}H n.m.r. spectrum contains individual signals of

both the O- and C-isomers while the spin–spin interaction is observed for the CH_2 protons coupled with magnetic isotopes of tin. Consequently, the mean lifetime of the isomers is above 10^{-1} sec in these conditions. The exchange between the O- and C-isomers is even faster in the presence of trialkylhalostannanes. When the stannane concentration is sufficiently high, no individual signals due to either the O- or the C-isomers can be observed in the ^1H n.m.r. spectrum which contains the averaged peaks. Thus, organotin derivatives of keto-enols are also subject to tautomeric (metallotropic) equilibria. These equilibria are fast, unlike those of the germanium derivatives of similar structure.

Recently we have discovered cases of metallotropic tautomery for organo-antimony compounds; at present they are being studied more thoroughly.

To sum up, the data discussed here lead to the problem of a quantitative or semi-quantitative approach which would permit a rationalization or even a prediction of the stability domains for the O- and C-isomeric species or for elementotropic tautomeric equilibria in organoelement derivatives of keto-enols or of related systems. We believe that further work in this direction will be both interesting and promising.

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