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Abstract

Full Text

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ON THE ELECTRONEGATIVITY OF THE PERFLUOROVINYL RADICAL

An estimate of the relative electronegativity of organic radicals follows most clearly from the reactivity of the corresponding organometallic compounds toward electrophilic agents. It was precisely by these methods that a series of electronegativities of organic radicals was established ([1]).

In an attempt to determine the place of the perfluorovinyl radical among other simplest organic radicals, we investigated the kinetics of decomposition by hydrogen chloride of perfluorodivinyl-, divinyl-, and diethylmercury in aqueous tetrahydrofuran

$$R_2Hg + HCl \rightarrow RHgCl + RH.$$

This process obeys a pseudo-first-order equation, and the reaction rate at 20° decreases in the series:

	$(CH_2{=}CH)_2Hg$	$(CF_2{=}CF)_2Hg$	$(C_2H_5)_2Hg$
$k,\ sec^{-1}$	$3.19 \cdot 10^{-4}$	$1.15 \cdot 10^{-4}$	$3.10 \cdot 10^{-5}$

Hexafluorodimethylmercury under these conditions does not react with hydrogen chloride or with sulfuric acid, despite the fact that the CF_3 radical is the most electronegative ([2]). If the reaction under discussion is regarded as a process of electrophilic substitution, then this fact, as well as the ratios of the rates of reaction with hydrogen chloride of the organomercury derivatives examined by us, finds its natural explanation in the greater or lesser electron density on the carbon atom bearing the metal.

Apparently, in divinyl- and perfluorodivinylmercury the carbon atom in the α-position, owing to conjugation of the π-electrons of the multiple bond with the $6p$ or $6d$ levels of the mercury atom, becomes so electron-donating that attack by a proton occurs rather readily. At the same time, because of the inductive influence of the fluorine atoms, the electron density at the α-carbon atom of the perfluorovinyl radical is lower than in the case of the vinyl radical; the density at the α-carbon atom of the ethyl radical and, evidently, of other saturated aliphatic radicals will be still lower. Finally, at the carbon atom of the trifluoromethyl radical, owing to the very strong inductive influence of the

fluorine atoms, the electron density becomes so small that attack by a proton is already practically impossible. On the contrary, nucleophilic attack on the mercury atom should proceed quite readily; indeed, hexafluorodimethylmercury, like perfluoromethylmercury halides, is very readily decomposed by alkali in the cold, with quantitative liberation of fluoroform.

On the basis of the considerations presented above, the fact is readily explained that, under the action of hydrogen chloride on $R_{nSn}(CF_3)_{4-n}$ (R = alkyl or aryl), cleavage of the alkyl or aryl (R) radical occurs, and not of the CF_3 group, whereas under the action of hydrogen chloride on $R_{nSn}(CF{=}CF_2)_{4-n}$ ($n = 2, 3$) cleavage of the perfluorovinyl radical occurs ([3]). From these positions it also becomes understandable that, in

upon the action of hydrogen chloride on phenyl(trichloromethyl)mercury, cleavage occurs not of the phenyl radical, but of the trichloromethyl radical. The lower electronegativity of chlorine accounts for the considerably smaller inductive effect of chlorine as compared with fluorine, and therefore for sufficient electron density at the carbon atom in the $Cl_3C{-}Hg$ grouping [4].

$$C_6H_5Hg \longrightarrow CCl_3$$

The order of cleavage of organic radicals from organometallic compounds is also retained for some other electrophilic reagents. Thus, in the decomposition of R_3SnCF_3 by chlorine or bromine, as in the case of decomposition by hydrogen chloride, cleavage occurs not of the trifluoromethyl radical, but of the alkyl radical [5]. Under the action of chlorine or bromine on $ClCH{=}CHHgCCl_3$, cleavage occurs not of the trichloromethyl radical, but of the β-chlorovinyl radical [6]. In this case, as in the case of the vinyl and perfluorovinyl derivatives considered above, the high electron density on the carbon atom of the β-chlorovinyl radical is apparently determined by the influence of the π-electrons of the multiple bond of the β-chlorovinyl radical.

By the action of perfluorovinylmagnesium bromide or iodide on alkylmercury halides, we obtained unsymmetrical organomercury compounds containing the perfluorovinyl radical. Thus, from vinyl-, ethyl-, and phenylmercury bromides, respectively, perfluorovinylvinyl-, perfluorovinylethyl-, and perfluorovinylphenylmercury were obtained. The structures of the compounds obtained were proved by the fact that, under the action of 10% HCl, vinyl-, ethyl-, and phenylmercury chlorides, respectively, were obtained in yields of about 80%, and at the same time in all cases, in practically quantitative yield, trifluoroethylene was obtained; moreover, in the reaction of perfluorovinylethyl- and perfluorovinylvinylmercury with $AsCl_3$, perfluorovinyldichloroarsine and, respectively, C_2H_5HgCl and $CH_2{=}CHHgCl$ were isolated in yields of more than 80% (Table 1).

Table 1

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Compound	Yield, %	B.p., °C/mm Hg	d_4^t	n_D^t	MR found	MR calc.	Reaction products of RHgR′ with HCl and $AsCl_3$
$CF_2{=}CF$ $CH_2{=}CH{>}Hg$	35	45/2	2.9510^{23}	1.5220^{23}	31.80	31.14	$CH_2{=}CHHgCl$[1] (82%) + $CF_2{=}CFH$ (99%)$CH_2{=}CHHgCl$[1] (81%) + $CF_2{=}CFAsCl_2$[3] (85%)
$CF_2{=}CF$ $C_2H_5{>}Hg$	30	53/12	2.7805^{24}	1.4711^{24}	31.16	31.49	$CH_2{=}CH_2HgCl$[1] (80%) + $CF_2{=}CFH$ (98%)C_2H_5HgCl[1] (81%) + $CF_2{=}CFAsCl_2$[3] (82%)
$CF_2{=}CF$ $C_6H_5{>}Hg$[2]	30	32/1	–	–	–	–	C_6H_5HgCl[1] (78%) + $CF_2{=}CFH$ (98%)

* In determining the melting points of mixed samples with specially prepared specimens: C_2H_5HgCl (m.p. 192°), $CH_2{=}CHHgCl$ (m.p. 182°), and C_6H_5HgCl (m.p. 271°), respectively, no depression is observed.

[2] $CF_2{=}CF$ $C_6H_5{>}Hg$ is extremely unstable and changes rapidly.

[3] B.p. 115°, n_D^{23} 1.4830 (according to the literature data for $CF_2{=}CFAsCl_2$: b.p. 115-116°, n_D^{20} 1.4825).

The liberation of trifluoroethylene, and not ethane, under the action of hydro-

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Fig. 1. Change in the rate of decomposition of organomercury compounds R_2Hg ($t = 20°$). 1 –rate of liberation of C_2H_6, $k = 3.19 \cdot 10^{-5}$; 2 –rate of liberation of $CF_2{=}CFH$, $k = 1.15 \cdot 10^{-4}$; 3 –rate of liberation of $CH_2{=}CH_2$, $k = 3.10 \cdot 10^{-4}$.

Figure 1: Fig. 1. Change in the rate of decomposition of organomercury compounds R_2Hg ($t = 20°$). 1 –rate of liberation of C_2H_6, $k = 3.19 \cdot 10^{-5}$; 2 –rate of liberation of $CF_2{=}CFH$, $k = 1.15 \cdot 10^{-4}$; 3 –rate of liberation of $CH_2{=}CH_2$, $k = 3.10 \cdot 10^{-4}$.

gen chloride on perfluorovinylethylmercury is in accordance with the rates of decomposition by hydrogen chloride of diethyl- and perfluorodivinylmercury. The liberation of trifluoroethylene, and not ethylene, under the action of hydrogen chloride on perfluorovinylvinylmercury can evidently be explained by conjugation

π-electrons of the multiple bond with the $6p$- or $6d$-levels of the mercury atom

$$CH_2{=}CH{-}Hg \rightarrow CF{=}CF_2.$$

As a result of this, a greater electron density arises on the α-carbon atom of the perfluorovinyl radical than on the α-carbon of vinyl. An analogous conjugation apparently also takes place in divinyldiperfluorovinylstannane, upon whose decomposition HCl likewise liberates trifluoroethylene ([3])

$$\begin{array}{c} CF{=}CF_2 \\ CH_2{=}CH{-}Sn \rightarrow CF{=}CF_2 \\ CH{=}CH_2 \end{array}$$

Experimental Part

Study of the kinetics of decomposition of organomercury compounds by hydrogen chloride

All organomercury compounds were prepared from the corresponding Grignard reagents and mercuric chloride or mercuric bromide in ether or tetrahydrofuran.

As the solvent for studying the kinetics of their decomposition by acids, a 15% solution of water in tetrahydrofuran containing 3.5% (0.957 mole/liter) hydrogen chloride was used. Before the experiment the solution was saturated with the same gas whose liberation was expected during decomposition of the organomercury compound under study. Saturation was carried out at the same temperature as in the subsequent decomposition experiment.

The reaction rate was characterized by the volume of gas evolved in a specified time.

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Fig. 1. Change in the rate of decomposition of organomercury compounds R_2Hg ($t = 20°$). 1 –rate of liberation of C_2H_6, $k = 3.19 \cdot 10^{-5}$; 2 –rate of liberation of $CF_2{=}CFH$, $k = 1.15 \cdot 10^{-4}$; 3 –rate of liberation of $CH_2{=}CH_2$, $k = 3.10 \cdot 10^{-4}$.

Unsymmetrical polysubstituted mercury derivatives containing the perfluorovinyl radical

Preparation (typical experiment). To an ethereal solution of $CF_2{=}CFMgJ$ or to a solution of $CF_2{=}CFMgBr$ in tetrahydrofuran (with a concentration of perfluorovinylmagnesium halide of about 0.1 mole in 100 ml of solvent), with vigorous stirring, an equimolecular solution of $RHgBr$ ($R = CH_2{=}CH{-}, C_2H_5{-}, C_6H_5{-}$) in the same solvents was added at $-10°$. After the addition of $RHgBr$, stirring was continued at 0° for 12 hr. The solvent was distilled off in vacuo, and the residue was subjected to distillation. The properties of the products obtained are given in Table 1.

Decomposition of $RHgR'$ by hydrochloric acid. Into a conical flask of 50 ml capacity, connected to a reflux condenser and an azotometer, were placed 10 ml of 10% HCl and a test tube containing a weighed portion of the organomercury compound; the reaction mixture was shaken vigorously. After completion of the vigorous reaction, the reaction mass was heated on a water bath until gas evolution ceased. The reaction vessel was thermostated, and the volume of gas evolved was reduced to normal conditions. Crystals separating from the solution were filtered off; after recrystallization, the melting point and the melting point of a mixed sample were determined. The data obtained are given in Table 1.

Reaction of $RHgR'$ with $AsCl_3$ (typical experiment). Into a small ampoule connected to a condenser was placed 0.9 g (0.0029 mo-

of $CF_2{=}CF{-}Hg{-}CH{=}CH_2$ and 0.53 g (0.0029 mole) of $AsCl_3$. After the vigorous reaction, accompanied by the separation of white crystals, had ended, the reaction mixture was heated for 2 hours on a water bath; the liquid reaction products were distilled off from the ampoule and subjected to repeated distillation. 0.53 g of $CF_2{=}CFAsCl_2$ was obtained, yield 85%. From the residue, 0.6 g of $CH_2{=}CHHgCl$ was isolated, yield 82%.

In an analogous manner, on interaction of $CF_2{=}CFHgC_2H_5$ and $AsCl_3$, $CF_2{=}CFAsCl_2$ and C_2H_5HgCl were obtained (see Table 1).

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