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Abstract

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A METHOD OF PAPER CHROMATOGRAPHY OF DIARYL ORGANOTIN COMPOUNDS AND ITS APPLICATION TO THE STUDY OF THE PRODUCTS OF THE REACTION OF UNSYMMETRICAL DIARYLIODONIUM SALTS WITH TIN DICHLORIDE

From the reaction mixture formed upon decomposition of a number of unsymmetrical diaryliodonium salts by tin powder in the presence of $SnCl_2$, we had previously isolated diaryl organotin compounds containing the more electron-accepting radicals ([1]). At the same time, the possibility was not excluded that the second, i.e., less electron-accepting, radical also passes onto tin. However, compounds with these radicals could have been formed in such small amounts that their isolation by ordinary methods would have been difficult. In order to clarify whether both radicals from unsymmetrical iodonium salts pass onto tin, we used, for analysis of the reaction mixture, a method developed by us for the chromatography of organotin compounds on paper. It should be noted that the literature contains no data on the application of the paper-chromatography method to the separation of diaryl organotin compounds. Therefore we first found conditions for the separation of known diaryl organotin compounds.

Known symmetrical diaryl organotin compounds were separated on paper (fast-filtering chromatographic paper of the Leningrad factory) impregnated with a 10% solution of olive oil in petroleum ether. Solutions of methyl alcohol in 1 N HCl served as the mobile phase. The chromatograms, dried in air, were developed with a saturated solution of diphenylcarbazone in 50% aqueous methyl alcohol. This reagent gives a purple coloration with diaryl organotin compounds. The values of the relative mobilities (Rf) of symmetrical organotin compounds are given in Table 1.

Table 1*

Values of Rf of symmetrical organotin compounds at various concentrations of CH_3OH in the mobile phase (at 20°C)

Ar_2SnCl_2	CH_3OH, %	CH_3OH, %	CH_3OH, %	CH_3OH, %	CH_3OH, %
	20	30	40	50	60
$(C_6H_5)_2SnCl_2$	0.33	0.40	0.50	0.60	–
$(n\text{-}CH_3C_6H_4)_2SnCl_2$	0.33	0.07	0.15	0.29	–
$(n\text{-}ClC_6H_4)_2SnCl_2$	0.04	0.10	0.19	0.34	–
$(n\text{-}BrC_6H_4)_2SnCl_2$	0.01	0.02	0.14	0.24	0.38
$(n\text{-}JC_6H_4)_2SnCl_2$	–	0.02	0.04	0.11	0.20
$(n\text{-}CH_3OC_6H_4)_2SnCl_2$	–	0.23	0.31	0.50	–
$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2$	0.18	0.29	0.48	0.70	–
$(m\text{-}C_2H_5OCOC_6H_4)_2SnCl_2$	0.23	0.38	0.55	0.75	–

* $SnCl_2$ and $SnCl_4$ in all cases have an Rf value of 0.80–0.90.

Further, upon decomposition of a mixture of two symmetrical diaryliodonium salts Ar_2JCl and Ar'_2JCl by tin dichloride, or (in the case where such iodonium salts were unavailable), by the reaction between two different symmetrical organomercury compounds Ar_2Hg and Ar'_2Hg with stannic chloride according to K. A. Kocheshkov and A. N. Nesmeyanov ([2]), mixtures were obtained containing unsymmetrical organotin compounds of the type $ArAr'SnCl_2$. The reaction products were separated by paper chromatography under the same conditions as the symmetrical organotin compounds. In this case, three spots were found on the chromatograms. In each case the upper and lower spots had the same R_f values as the corresponding symmetrical organotin compounds applied to the same chromatogram. The middle spot evidently corresponded to the unsymmetrical diaryltin organotin compound. The R_f values thus obtained for the unsymmetrical diaryltin organotin compounds are given in Table 2.

Table 2

R_f values of unsymmetrical diaryltin organotin compounds at different concentrations of methyl alcohol in the mobile phase

$ArAr'SnCl_2$	CH_3OH, %	CH_3OH, %	CH_3OH, %	CH_3OH, %
	20	30	40	50
$(n\text{-}ClC_6H_4,\ C_6H_5)\ SnCl_2$ *	–	0.20	0.33	0.45
$(n\text{-}BrC_6H_4,\ C_6H_5)\ SnCl_2$ *	–	0.11	0.22	0.39
$(n\text{-}JC_6H_4,\ C_6H_5)\ SnCl_2$ **	0.05	0.11	0.20	0.34
$(n\text{-}CH_3OC_6H_4,\ C_6H_5)\ SnCl_2$ *	–	0.31	0.42	–
$(n\text{-}C_2H_5OCO,\ C_6H_4,\ n\text{-}CH_3OC_6H_4)SnCl_2$ **	–	0.39	0.62	

ArAr′$SnCl_2$	CH_3OH, %	CH_3OH, %	CH_3OH, %	CH_3OH, %
(*n*-$C_2H_5OCOC_6H_4$, C_6H_5)$_2SnCl_2$ **	–	–	–	–
(*n*-$C_2H_5OCOC_6H_4$, *n*-$CH_3C_6H_4$) $SnCl_2$ **	0.15	0.29	–	–
(*m*-$C_2H_5OCOC_6H_4$, *n*-$CH_3C_6H_4$) $SnCl_2$ *	0.18	0.32	–	–

* The compound was obtained by decomposition of a mixture of two symmetrical iodonium salts.
** The compound was obtained by the method of Nesmeyanov and Kocheshkov ([2]) by interaction of two symmetrical organomercury compounds.

The method of paper chromatography was applied to the analysis of diaryltin organotin compounds formed during the decomposition of unsymmetrical iodonium salts by stannic chloride. The reaction was carried out in two different ways: 1) in the presence of metallic tin powder in acetone (the conditions described in our previous work ([1])) and 2) without metallic tin, in alcohol *.

For identification of the organotin compounds formed, a mixture of the corresponding symmetrical and unsymmetrical compounds, prepared by the method described above, was applied to the chromatogram as a reference. It was found that in both cases, both with metallic tin and without it, the same mixtures of organotin compounds are formed; the results of the analysis of these mixtures are given in Table 3. As can be seen from this table, only in the decomposition of chloro *m*-carbethoxydiphenyliodonium does one radical from the unsymmetrical diaryliodonium salt pass to tin. In all other cases, both radicals of the unsymmetrical iodonium salt passed to tin to one degree or another. By the method of quantitative paper chromatography (elution of the spots with a solution of diphenylcarbazone in *n*-xylene and colorimetry at λ 550 Å), the ratio of the amounts of organotin compounds formed during the decomposition of unsymmetrical diaryliodonium salts was studied. The results are presented in Table 3.

The data obtained indicate that the dependence of the degree of transfer of one or another radical from an unsymmetrical iodonium salt to tin on its structure is complex in character and depends comparatively little on its electron-donating or electron-accepting properties.

* We had previously shown that, upon decomposition of a number of symmetrical iodonium salts by stannic chloride in alcohol, symmetrical diaryltin organotin compounds are obtained in good yield:

$$2Ar_2JCl + 2SnCl_2 \rightarrow Ar_2SnCl_2 + SnCl_4 + 2ArJ.$$

Table 3

Results of chromatographic analysis of mixtures of organotin compounds formed during decomposition of unsymmetrical diaryliodonium salts both with stannous chloride and with tin powder in the presence of stannous chloride

Initial diaryliodonium salt	Formed organotin compounds and their ratios (in parentheses)	Formed organotin compounds and their ratios (in parentheses)	Formed organotin compounds and their ratios (in parentheses)
$\left\langle \begin{matrix} n\text{-}ClC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}ClC_6H_4)_2SnCl_2(1)$	$\left\langle \begin{matrix} n\text{-}ClC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle SnCl_2(2)$	$(C_6H_5)_2SnCl_2(1)$
$\left\langle \begin{matrix} n\text{-}BrC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}BrC_6H_4)_2SnCl_2(1)$	$\left\langle \begin{matrix} n\text{-}BrC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle SnCl_2(2)$	$(C_6H_5)_2SnCl_2(1)$
$\left\langle \begin{matrix} n\text{-}JC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}JC_6H_4)_2SnCl_2(1)$	$\left\langle \begin{matrix} n\text{-}JC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle SnCl_2(2)$	$(C_6H_5)_2SnCl_2(1)$
$\left\langle \begin{matrix} n\text{-}CH_3OC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}CH_3OC_6H_4)_2SnCl_2(0,5)$	$\left\langle \begin{matrix} n\text{-}CH_3OC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle SnCl_2(2)$	$(C_6H_5)_2SnCl_2(1)$
*			
$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ CH_3OC_6H_4 \end{matrix} \right\rangle JCl$	$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2(1)$	$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ n\text{-}CH_3OC_6H_4 \end{matrix} \right\rangle SnCl_2(2)$	$(n\text{-}CH_3OC_6H_4)_2SnCl_2(0,25)$
*			
$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2(1)$	$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle SnCl_2(2)$	$(C_6H_5)_2SnCl_2(0,5)$
$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ n\text{-}CH_3C_6H_4 \end{matrix} \right\rangle JCl$	$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2(0,2)$	$\left\langle \begin{matrix} n\text{-}C_2H_5OCOC_6H_4 \\ n\text{-}CH_3C_6H_4 \end{matrix} \right\rangle SnCl_2(2)$	$(n\text{-}CH_3C_6H_4)_2SnCl_2$
$\left\langle \begin{matrix} m\text{-}C_2H_5OCOC_6H_4 \\ C_6H_5 \end{matrix} \right\rangle JCl$	$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2$	No other compounds were detected	No other compounds were detected
$\left\langle \begin{matrix} m\text{-}C_2H_5OCOC_6H_4 \\ n\text{-}CH_3C_6H_4 \end{matrix} \right\rangle JCl$	$(n\text{-}C_2H_5OCOC_6H_4)_2SnCl_2(0,7)$	$\left\langle \begin{matrix} m\text{-}C_2H_5OCOC_6H_4 \\ n\text{-}CH_3C_6H_4 \end{matrix} \right\rangle SnCl_2(2)$	$(n\text{-}CH_3C_6H_4)_2SnCl_2(1)$

* The determination was carried out one hour after the start of the reaction. After 24 hours, only insignificant amounts of organotin compounds containing anisyl radicals were found in the reaction mixture.

It should be noted that tin compounds containing an anisyl radical have low stability and decompose in the reaction medium. This explains the results obtained in our previous work ([1]) on the decomposition of unsymmetrical diaryliodonium salts by stannous chloride, since all the starting unsymmetrical iodonium salts (with the exception of chlorinated *n*-carbethoxydiphenyliodonium), the decomposition of which we studied, contained an *n*-anisyl radical. The anisyl organotin compounds apparently decomposed both during the reaction itself and during the processing of the reaction mixture. Only the more stable organotin compounds with a more electron-accepting radical were isolated.

Experimental Part

Procedure for analyzing a mixture of diaryl organotin compounds by paper chromatography

Chromatographic paper (Leningrad factory, fast-filtering) was impregnated with a 10% solution of olive oil in petroleum ether. After evaporation of the petroleum ether, solutions of diaryl organotin compounds in methyl alcohol (1-10γ) were applied to it. Solutions of methyl alcohol in 1N HCl were used for separation. Chromatography was carried out by the ascending method; the travel length of the solvent front was 20-50 cm. The chromatogram was then dried in air for 2-3 hours or with a stream of hot air and sprayed with a saturated solution of diphenylcarbazone in 50% aqueous methyl alcohol. The diaryl organotin compounds appeared as purple spots. After the chromatogram dried, the spots faded, but appeared again when the chromatogram was moistened with water. The minimum detectable amounts for $(C_6H_5)_2SnCl_2$ were 0.5γ; the optimum amounts were 5-10γ.

Determination of the ratio of diaryl organotin compounds formed in the interaction of unsymmetrical iodonium salts with stannous chloride

Onto a strip of chromatographic paper 10-20 cm wide and 30-50 cm long, 2-4 samples were applied in the form of strips approximately 1 cm wide. After separation, part of the chromatogram with the first sample was used to determine the position of the spots of organotin compounds. Then, from the still-moist chromatogram (after 5-7 minutes of drying in air), sections containing the separated organotin compounds were cut out and placed in colorimetric test tubes with 6 ml of a saturated solution of diphenylcarbazone in n-xylene. The intensity of the resulting purple coloration was measured after 24 hours on an SF-4 spectrophotometer at a wavelength $\lambda = 550$ Å.

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