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Abstract

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PHENYLMERCURY DERIVATIVES OF SUBSTITUTED
2-PHENYLSULFONYLAMINOPYRIDINES ==================================

(Presented by Academician A. N. Nesmeyanov on 29 X 1964)

It was found earlier that arylmercury derivatives of nitrosophenols are tautomeric in solution ([1]). In light of this, it seemed of interest to investigate the structure in solution of C_6H_5Hg-derivatives of tautomeric 2-arylsulfonylaminopyridines ([2]–[5]). Only one paper discusses possible structures for organometallic compounds of this type, but it gives no experimental evidence in favor of one structure or another ([6]).

Table 1

Compound	Yield, %	M.p. (decomp.), °C	C, % found	C, % calc.	H, % found	H, % calc.	Hg, % found	Hg, % calc.
[structural formula: pyridine ring bearing $N(SO_2\text{-}C_6H_4R)(HgC_6H_5)$; $R = H$]	92	168-170from C_2H_5OH	40.04	39.96	2.79	2.76	38.72	39.26
$R =$ CH_3	92	185-186from C_2H_5OH	41.03	41.19	3.09	3.07	37.84	38.20
$R =$ CH_3O	90	168-169from C_2H_5OH	40.02	39.97	3.08	2.98	37.22	37.07
$R =$ Cl	96	157-159from C_2H_5OH	37.54	37.43	2.45	2.40	36.64	36.78

Compound	Yield, %	M.p. (decomp.), °C	C, % found	C, % calc.	H, % found	H, % calc.	Hg, % found	Hg, % calc.
R = NO_2	98	156-157from $C_5H_5N{-}H_2O$	36.57	36.72	2.42	2.36	35.89	36.08
[structural formula: naphthalene derivative, $N(SO_2C_6H_5)(HgC_6H_5)$]	98	176-177from $CH_3C_6H_5$	47.00	47.19	3.16	3.05	35.66	35.83

Phenylmercury derivatives were obtained by the action of C_6H_5HgOH on arylsulfonylaminopyridines (Table 1). The C_6H_5Hg group in them is bonded to one of the nitrogen atoms, which is confirmed by their cleavage into phenylmercury halide and the K derivative of arylsulfonylaminopyridine under the action of KI and KBr, as well as by the absence of the ability to form a K salt under the action of KOH. Consequently, a priori, either an aminopyridine or a pyridonimine structure is possible for them:

[pyridine structure: $N(SO_2C_6H_5)(HgC_6H_5)$] [pyridonimine structure: $=NSO_2C_6H_5,\ NHgC_6H_5$]

Determination of the structure of the C_6H_5Hg-derivatives in solution was carried out on the basis of absorption spectra, using as a criterion the characteristic maximum of the imino form in the region of 325 mμ ([2], [5]). Preliminarily, using the example of the C_6H_5Hg-derivative of N-phenylsulfonyl-α-naphthylami-

It was found that replacement of hydrogen by a C_6H_5Hg group does not change the shape of the spectral curve in the region 260–340 m and only slightly affects the position of the absorption maximum and its intensity. Thus, in dioxane, for the free compound and the C_6H_5Hg derivative, respectively: $\lambda_{\text{max}} = 289$ m, $\varepsilon_{\text{max}} = 7400$ and $\lambda_{\text{max}} = 292$ m, $\varepsilon_{\text{max}} = 8100$. It was also found that, when the structure is fixed, the shape of the spectral curve of the C_6H_5Hg derivative does not depend on the nature of the solvent.

Fig. 1. Absorption spectra in acetonitrile: **1** –1-methyl-2-phenylsulfonyliminopyridine. **2** –2-$C_5H_4NH(R)SO_2C_6H_5$, $R = CH_3$, **3** –R = Na, **4** –$R = C_6H_5Hg$

Fig. 2. Absorption spectra in $C_4H_8O_2$: **1** –1-methyl-2-phenylsulfonyliminopyridine. **2** –2-$C_5H_4NN(R)SO_2C_6H_5$, R = H. **3** –$R = C_6H_5Hg$; **4** –2-$C_5H_4NN(R)SO_2C_6H_5$,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

R = C_6H_5Hg, in CH_3CN; **5** –the same in $HCON(CH_3)_2$; **6** –the same in C_5H_5N

Comparison of the spectrum of the C_6H_5Hg derivative of 2-phenylsulfonylaminopyridine in such a strongly polar solvent as acetonitrile with the spectra of the isomeric methyl derivatives and the Na salt (Fig. 1) shows that in this case it cannot be assigned the structure of either of the limiting isomeric forms or an ionic structure. The presence in the spectrum of the C_6H_5Hg derivative of absorption in the region of 325 m , characteristic of the pyridonimine form, whose intensity is greatly reduced and does not depend on concentration or on addition of C_6H_5HgOH to the solution (which rules out the possibility of hydrolysis), should be interpreted as the result of the presence in solution of two forms: the aminopyridine and pyridonimine forms. From Fig. 2 it is seen that ε of the maximum in the region of 325 m depends substantially on the nature of the solvent, and in weakly polar solvents of the dioxane type it disappears altogether. Obviously, as for the free compound, this indicates mutual interconversion of the two forms as a result of tautomeric equilibrium:

[[structural formula: aminopyridine form with $SO_2C_6H_5$ and HgC_6H_5 substituents]] $\rightleftharpoons$ [[structural formula: p

Thus, for example, in dioxane, in contrast to acetonitrile, the phenylmercury derivative exists practically entirely in the aminopyridine form. At the same time, its maximum is characterized by a bathochromic shift of 20 m compared with the maximum of the aminopyridine form of the free compound and by a 23% decrease in intensity. This effect is probably caused

with formation of a coordination bond of the C_6H_5Hg-group with the heterocyclic nitrogen atom:

pyridine ring bearing $N(SO_2C_6H_5)(HgC_6H_5)$
and a dotted coordination bond from the ring $N \cdots Hg$

analogous to that existing in the C_6H_5Hg-derivative of 8-oxyquinoline (7). Examination of Stuart–Briegleb models shows that, upon rotation of the

$$-N\begin{matrix}SO_2C_6H_5\\HgC_6H_5\end{matrix}$$

group about the $C—N$ bond, overlap of the van der Waals radii of the mercury atom and the heterocyclic nitrogen is possible, whereby favorable conditions are created for the formation of a four-membered chelate ring.

Proceeding from the content of the pyridonimine form in various solvents at 20° (found by comparing $\varepsilon_{\max}$ of the pyridonimine form with $\varepsilon_{\max}$ of the methylated standard), it may be concluded that for 2-phenylsulfonylaminopyridine the pyridonimine form is more stable than for its C_6H_5Hg-derivative, especially in low-polar solvents (Table 2). According to the data for solutions in aliphatic nitriles, with decrease of the dielectric constant in a series of solvents of one chemical type, the content of the pyridonimine form falls more rapidly for the C_6H_5Hg-derivative than for phenylsulfonylaminopyridine.

Fig. 3. Dependence of pK_T in pyridine on σ_n for 2-arylsulfonylaminopyridines (B) and their phenylmercury derivatives (A)

Table 2

Solvent	Dielectric constant	Content of imino form, %, pyridine ring $N(SO_2C_6H_5)(HgC_6H_5)$	Content of imino form, %, pyridine ring $NHSO_2C_6H_5$
Acetonitrile	37.5	34	35
Propionitrile	27.2	11	27
Butyronitrile	20.3	3.7	25
Isocapronitrile	15.5	2.2	22
Dimethylformamide	36.7	13	33
Dimethyl sulfoxide	–	17	46
Pyridine	12.3	8.6	14
1,2-Dichloroethane	10.3	1.2	30
Ethyl acetate	6.0	0.9	11
Tetrahydrofuran	7.5	0.9	5.5
Dioxane	2.2	0.3	4.1

Determination of the constants of tautomeric equilibrium in pyridine for para-substituted 2-phenylsulfonylaminopyridines and their phenylmercury derivatives shows that in both cases (Fig. 3) a linear dependence of pK_T on the Hammett constant σ_n for the corresponding substituent is observed (by the tautomeric-equilibrium constant is meant the ratio of the concentrations in solution of the pyridonimine and aminopyridine forms for the given compound).

On the basis of the parallelism of the corresponding straight lines, it may be asserted that polar factors influence in the same way the position of the tautomeric equilibrium of 2-arylsulfonylaminopyridines and their C_6H_5Hg-derivatives.

Thus, the results obtained show that even when like-named atoms are present at the ends of the tautomeric system, the position of equilibrium is not the same for migrating groups of different nature and is determined not only by the relative stability of the two electromeric forms of the common anion and by the relative stability of the covalent bonds formed by the departing cation with each of them (^{8}). Solvation and chelation effects may also play an important role. At the same time, the effect on the position of tautomeric equilibrium of polar effects that influence only the relative stability of the electromeric forms of the common anion apparently does not depend on the nature of the migrating group.

In conclusion, I take this opportunity to express my deep gratitude to Academician A. N. Nesmeyanov for his attention to the work.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.