CHEMISTRY

1960

SovietRxiv

Abstract

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CHEMISTRY

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STRUCTURE OF ARYLMERCURY DERIVATIVES OF NITROANILINES AND NITRONAPHTHYLAMINES

(Presented by Academician A. N. Nesmeyanov, September 16, 1959)

For mercury, the formation of strong nonionogenic bonds with carbon, sulfur, and to some extent nitrogen is characteristic. This property is manifested, for example, in the case of mercury derivatives of ketoenols and isatin, which are respectively C- and N-derivatives. Alkali metals (and many others) in this case form O-derivatives ([1–4]). The behavior of mercury bound to molecules of other tautomeric and pseudomeric systems is of definite interest, especially in view of the fact that, in essence, metallotropic tautomerism is unknown. The question is complicated by the fact that mercury in the form of oxide salts readily mercurates the aromatic nucleus, leaving the tautomeric system ([5]).

Salts and even hydroxides of arylmercury possess a greatly reduced mercurating ability ([6]). As a consequence, we undertook a study of arylmercury derivatives of a series of tautomeric and pseudomeric systems.

As the first example, the pseudomeric system of nitroaniline was chosen. Mercury derivatives of nitroanilines not containing mercury bound to the aromatic nucleus were first obtained by Jackson and Piks ([7]), and subsequently by Kharasch and co-workers ([8]). Jackson and Piks regarded them as N-derivatives of nitroanilines; however, Kharasch, proceeding from the bright coloration of the compounds obtained, assigned to them the structure of quinoniminenitro compound salts. By the reaction of arylmercury hydroxides with nitroanilines and nitronaphthylamines, their arylmercury derivatives were obtained according to the general scheme

$$\mathrm{RHgOH} + \mathrm{HA} \rightarrow \mathrm{RHgA} + \mathrm{H_2O},$$

where $R = \mathrm{C_6H_5}-$, 4-$(\mathrm{CH_3})_2\mathrm{NC_6H_4}-$, and HA is nitroaniline or nitronaphthylamine, see Table 1.

Fig. 1

Arylmecury acetates do not react with nitroanilines even upon prolonged heating. The compounds obtained are brightly colored crystalline substances soluble

Fig. 1

Figure 1: Fig. 1

in organic solvents. They are unchanged by the action of hot alkalis, but are readily decom-

Table 1

No.	R	R′	M.p. (decomp.), °C	Yield, %	C found	C calc.	H found	H calc.	N found	N calc.	Hg found	Hg calc.
1	C_6H_5 —	p-$NO_2C_6H_4$ —	209, from amyl alcohol	88	34.65	34.73	2.39	2.43	6.91	6.75		
2	C_6H_5 —	o-$NO_2C_6H_4$ —	197, from benzene	75	34.62	34.73	2.51	2.43	6.76	6.75		
3	C_6H_5 —	dinitro-C_6H_3 —	242, from amyl alcohol	87	31.28	31.38	1.95	1.97	9.26	9.15		
4	$(CH_3)_2$- —	p-NC_6H_4-$NO_2C_6H_4$ —	189, from alcohol	88	36.59	36.72	3.34	3.30	8.90	9.18		
5	$(CH_3)_2$- —	o-NC_6H_4-$NO_2C_6H_4$ —	176, from benzene	91	36.75	36.72	3.34	3.30	9.11	9.18		
6	$(CH_3)_2$- —	dinitro-NC_6H_4-C_6H_3 —	215, from amyl alcohol	92	33.50	33.43	2.86	2.80	10.90	11.14		

No.	R	R′	M.p. (decomp.), °C	Yield, %	C found	C calc.	H found	H calc.	N found	N calc.	Hg found	Hg calc.
7	$(CH_3)_2NC_6H_4$–	1-nitronaphthyl-2–	136, fapht	90	42.50	42.55	3.46	3.37	8.39	8.27	39.49	39.48
				xylene								
8	$(CH_3)_2NC_6H_4$–	1-nitronaphthyl-2–	195, fapht	73	42.49	42.55	3.49	3.37	8.45	8.27	39.28	39.48
				toluene								
9	$(CH_3)_2NC_6H_4$–	1-nitronaphthyl-2–	213, fapht	96	42.68	42.55	3.41	3.37	8.22	8.27	39.68	39.48
				toluene								

Table 2

Compound	Solvent	νmax, $cm^{-1} \cdot 10^{-3}$	ϵmax
$H_2NC_6H_4NO_2$-2	C_2H_5OH	24.7	4460
$H_2NC_6H_4NO_2$-2	C_2H_5OH	36.0	4230
$C_6H_5HgNHC_6H_4NO_2$-2	Same	25.0	4500
$C_6H_5HgNHC_6H_4NO_2$-2	Same	36.2	3800
$(CH_3)_2NC_6H_4HgNHC_6H_4NO_2$-2	Same	24.5	4800
$(CH_3)_2NC_6H_4HgNHC_6H_4NO_2$-2	Same	36.5	20000
$C_6H_5NHC_6H_4NO_2$-2	Same	23.5	4760
$C_6H_5NHC_6H_4NO_2$-2	Same	38.5	9800
$C_6H_5CH_2NHC_6H_4NO_2$-2	Same	23.5	5000
$C_6H_5CH_2NHC_6H_4NO_2$-2	Same	35.5	4000
1-$H_2NC_{10}H_6NO_2$-4	$CH_3COOC_2H_5$	25.0	12000
1-$H_2NC_{10}H_6NO_2$-4	$CH_3COOC_2H_5$	38.5	8000

Compound	Solvent	νmax, $cm^{-1} \cdot 10^{-3}$	ϵmax
1-$(CH_3)_2NC_6H_4HgNHC_{10}H_6NO_2$-4	Same	24.6	12700
1-$(CH_3)_2NC_6H_4HgNHC_{10}H_6NO_2$-4	Same	37.6	21000
1-$H_2NC_{10}H_6NO_2$-2	C_2H_5OH	22.8	6400
1-$H_2NC_{10}H_6NO_2$-2	C_2H_5OH	36.0	11500
1-$(CH_3)_2NC_6H_4HgNHC_{10}H_6NO_2$-2	Same	23.0	6600
1-$(CH_3)_2NC_6H_4HgNHC_{10}H_6NO_2$-2	Same	36.4	27500
2-$H_2NC_{10}H_6NO_2$-1	$CH_3COOC_2H_5$	24.7	4500
2-$H_2NC_{10}H_6NO_2$-1	$CH_3COOC_2H_5$	31.2	3700
2-$H_2NC_{10}H_6NO_2$-1	$CH_3COOC_2H_5$	38.2	10500
2-$(CH_3)_2NC_6H_4HgNHC_{10}H_6NO_2$-1	Same	25.0	5200
$C_6H_5HgOCOCH_3$	C_2H_5OH	37.8	75
$C_6H_5HgOCOCH_3$	C_2H_5OH	38.7	90
$C_6H_5HgOCOCH_3$	C_2H_5OH	39.7	75

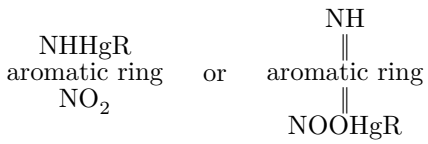
are decomposed by solutions of dilute mineral acids, potassium iodide, and sodium sulfide with the formation of arylmercury compounds and free nitroanilines. Consequently, the arylmercury radical in them is not bonded to the aromatic nucleus of the nitroaniline, and they may have the structure either of N-derivatives or of salts of quinone-imine nitro compounds:

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3



To resolve this question, absorption spectra were recorded for the substances obtained and for the starting compounds, as well as for N-benzyl and phenyl derivatives of nitroanilines (Figs. 1–3 and Table 2)*.

Fig. 2

The spectra of the compounds obtained show great similarity to the spectra of the corresponding nitroanilines and nitronaphthylamines, and the positions of the principal maxima practically coincide with their positions in the spectra of the starting compounds. The absorption curves of the phenylmercury derivatives are, in their shape, analogous to the spectra of nitroanilines because the intrinsic absorption of the phenylmercury radical is very weak and has little effect on the spectrum of nitroaniline. The difference in the short-wavelength region from the spectra of the starting compounds, observed in the case of dimethylaminophenylmercury derivatives, is caused by superposition upon the nitroaniline spectrum of the intrinsic intense absorption of the dimethylaminophenylmercury radical. The latter increases considerably under the influence of the nitroaniline residue. We observed the same phenomenon on passing from dimethylaminophenylmercury acetate to bis-dimethylaminophenylmercury (see Fig. 3). Despite the indicated differences, the invariance of the band shape and of the position of the principal maximum indicates that the compounds obtained are N-derivatives of nitroanilines and nitronaphthylamines.

Fig. 3

It is known that introduction of electron-donating substituents into the amino group of nitroanilines leads to a bathochromic shift and an increase in the absorption intensity of the principal maximum, whereas introduction of electron-accepting substituents causes a hypsochromic shift and a decrease in absorption intensity ([9–12]). The invariance of the position of the principal maximum in the spectra of nitroanilines upon introduction of an arylmercury substituent into the amino group

* The absorption spectra were recorded on a spectrovisor in the Optical Laboratory of INEOS, Academy of Sciences of the USSR.

indicates that the arylmercury radical, as a pseudoatom, exhibits a greater similarity to the hydrogen atom with respect to its influence on the chromophoric system of nitroaniline. On the basis of work ([13]), which establishes a connection between the absorption of substituted benzenes and the Hammett constant σ of the corresponding substituent, it may be assumed that this similarity is of a more general character, extending also to the inductive effect of the arylmercury radical.

From consideration of the intensity of the principal maximum in the spectra of arylmercury derivatives it follows that the phenylmercury radical possesses weak electron-acceptor properties, while the dimethylaminophenylmercury radical may exhibit both weak electron-acceptor and weak electron-donor properties. Comparison of the spectra of phenylmercury derivatives with the spectra of N-benzyl- and phenyl-substituted nitroanilines shows that the phenylmercury radical is by its nature opposite to the benzyl radical, and that its electron-acceptor properties are more strongly expressed than those of the phenyl radical.

In conclusion we express our deep gratitude to Academician A. N. Nesmeyanov and I. V. Obreimov for their attention to this work.

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Received
10 IX 1959

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