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Abstract

Full Text

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p-DIMETHYLAMINOPHENYLMERCURY DERIVATIVES OF OXYAZO COMPOUNDS AND PHENYLHYDRAZONES OF QUINONES

It has now been established that arylazophenols of the *o*- and *p*-series, both in solution and in the solid state, have an oxyazo structure ([1]–[3], [4]). 4-Arylazo-1-naphthols and 1-arylazo-2-naphthols are tautomeric in solution ([1], [5]–[9]), whereas oxyazo compounds of the anthracene and acenaphthene series are phenylhydrazones of quinones ([5], [10])

$HO–C_6H_4– N=NC_6H_5$ ⇄ [[structural formula of naphthoquinone phenylhydrazone tautomer]] [[s

Smith and Mitchell showed that arylazophenols are mercurated by mercuric acetate, but much more difficultly than the corresponding phenols ([11]). They did not succeed in mercurating 1-phenylazo-2-naphthol and 4-phenylazo-1-naphthol ([12]).

Fig. 1. Absorption spectra of solutions in ethyl acetate: *a* –R = H; *b* –R = CH_3; *c* –R = 4-$(CH_3)_2NC_6H_4Hg$

Up to now, mercury derivatives of oxyazo compounds that are not products of mercuration into the aromatic nucleus have not been obtained.

In continuation of previous work ([13]–[15]), we studied the interaction of *p*-dimethylaminophenylmercuric hydroxide with a series of oxyazo compounds and phenylhydrazones of quinones, and also with benzil phenylhydrazone. In all cases, upon reaction in methanolic solution, the corresponding arylmercury derivatives were obtained according to the general scheme:

$$(CH_3)_2NC_6H_4HgOH + HA \rightarrow (CH_3)_2NC_6H_4HgA + H_2O,$$

where HA is an oxyazo compound or a phenylhydrazone of a quinone; see Table 1.

The compounds obtained are crystalline substances of dark-yellow or red color, insoluble in water, soluble in organic solvents, and melting with decomposition. Derivatives of *o*-oxyazo compounds exhibit chelate properties, being very readily soluble in nonpolar solvents, for example in benzene. Arylmercury derivatives of *p*- and *o*-oxyazo compounds are cleaved, respectively, by the action of NaOH or C_2H_5ONa, with formation of the sodium derivative of the oxyazo compound and arylmercury hydroxide or alcoholate, identified in the form of a derivative of *o*-nitroaniline:

$$(CH_3)_2NC_6H_4HgA + NaOH \rightarrow (CH_3)_2NC_6H_4HgOH + NaA,$$

$(CH_3)_2NC_6H_4HgOH$+[[structural formula of *o*-nitroaniline]] → [[structural formula of *N*-(*p*-dimethylaminophe

Derivatives of phenylhydrazones of quinones are cleaved by the action of potassium iodide:

$$(CH_3)_2NC_6H_4HgA + KJ + H_2O \rightarrow (CH_3)_2NC_6H_4HgJ + KOH + HA.$$

Table 1

$(CH_3)_2NC_6H_4HgA$

A	m.p., °C (solvent)	Yield, %	C, % found	C, % calculated	H, % found	H, % calculated	N, % found	N, % calculated	Hg, % found	Hg, % calculated
p-$RC_6H_4N{=}NC_6H_4O$—, $R{=}H$	160 from C_6H_6	83	46.59; 46.53	46.36	3.62; 3.65	3.70	8.24; 8.32	8.11	–	38.73
p-$RC_6H_4N{=}NC_6H_4O$—, $R{=}CH_3$	164 from C_6H_6	83	47.65; 47.58	47.41	4.16; 4.03	3.98	8.20; 8.16	7.90	–	37.71

A	m.p., °C (solvent)	Yield, %	C, % found	C, % calculated	H, % found	H, % calculated	N, % found	N, % calculated	Hg, % found	Hg, % calculated
p-$R C_6H_4N{=}NC_6H_4O$—, $R{=}CH_3$	178 from C_6H_6	81	46.21; 46.05	46.02	3.83; 3.88	3.86	7.74; 7.80	7.67	—	38.61
p-$R C_6H_4N{=}NC_6H_4O$—, $R{=}NO_2$	189 from $C_5H_{11}OH$	78	42.67; 42.71	42.75	3.35; 3.31	3.22	9.72; 9.82	9.95	—	35.63
o-oxyazo compound, CH_3-substituted ring, $R{=}H$	139 from C_2H_5OH	87	47.43; 47.50	47.41	3.99; 4.13	3.98	8.08; 8.04	7.90	37.57; 37.81	37.71
o-oxyazo compound, CH_3-substituted ring, $R{=}CH_3$	129 from C_2H_5OH	78	48.46; 48.43	48.38	4.23; 4.26	4.24	7.74; 7.84	7.70	36.72; 36.63	36.74
o-oxyazo compound, CH_3-substituted ring, R—CH_3O	158 from C_2H_5OH	88	47.25; 47.30	47.01	4.28; 4.23	4.12	7.91; 7.74	7.48	35.06; 35.35	35.69
o-oxyazo compound, CH_3-substituted ring, $R{=}NO_2$	172 from C_2H_5OH	69	43.74; 43.89	44.05	3.51; 3.50	3.49	10.05; 10.18	9.71	34.88; 35.26	34.77

A	m.p., °C (solvent)	Yield, %	C, % found	C, % calculated	H, % found	H, % calculated	N, % found	N, % calculated	Hg, % found	Hg, % calculated
Quinone phenylhydrazone derivative, NN—C_6H_5	136 from C_2H_5OH	88	54.17; 54.37	54.42	3.56; 3.54	3.75	6.60; 6.65	6.80	32.06; 32.10	32.46
Quinone hydrazone derivative, O= ring =NN(C_6H_5)(C_6H_5)	184 from C_4H_9OH	91	52.87; 53.04	52.74	3.67; 3.65	3.58	6.92; 7.15	7.10	33.48; 33.50	33.88
Quinone hydrazone derivative, $C_6H_5COC_6H_5$, NN(C_6H_5)(C_6H_5)	193 from C_4H_9OH	91	54.52; 54.43	54.23	4.11; 4.14	4.06	7.08; 7.15	6.77	32.10; 32.08	32.35

Consequently, the arylmercury radical in the compounds obtained is not bound to the aromatic nucleus of the oxyazo compound or quinone phenylhydrazone, but replaces the labile hydrogen atom.

Thus, arylmercury derivatives may have either a benzenoid or a quinoid structure, for example:

$$\mathrm{RHgO{-}C_6H_4{-}N{=}NC_6H_5} \qquad \mathrm{O{=}C_6H_4{=}NN}\begin{pmatrix}\mathrm{C_6H_5}\\ \mathrm{HgR}\end{pmatrix}$$

To resolve this question, absorption spectra were recorded for solutions of the compounds obtained, the corresponding oxyazo compounds and quinone phenylhydrazones, and their methyl derivatives in ethyl acetate in the region 20 000—40 000 cm^{-1}, see Figs. 1—3*.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The absorption spectra of the arylmercury oxyazo compounds of the *p*- and *o*-series are similar to the spectra of the starting compounds and their methyl ethers. The form of the spectral curve in the region 20 000—33 000 cm^{-1} is practically unchanged on passing from the oxyazo compound to the arylmercury derivative. The appearance of an additional maximum in the region 33 000—40 000 cm^{-1} is due to the intrinsic absorption of the dimethylaminophenylmercury radical ([13]). The rather considerable decrease in the intensity of absorption of the maximum at 32 000 cm^{-1} in the spectrum of the methyl ether of phenylazo-1,4-cresol is a consequence of the methylation effect ([16]). The indicated differences in the intensities of the absorption maxima do not exert a substantial influence on the overall similarity of the shape of the spectral curve of the arylmercury derivatives, the oxyazo compounds, and their methyl ethers; on this basis one may conclude that the arylmercury derivatives have a benzenoid structure in solution.

Fig. 2. Absorption spectra of solutions in ethyl acetate:
a–$R = H$; b–$R = CH_3$; v–$R = 4\text{-}(\mathrm{CH}_3)_2NC_6H_4Hg$

Fig. 3. Absorption spectra of solutions in ethyl acetate:
a–$R = H$; b–$R = CH_3$; v–$R = 4\text{-}(\mathrm{CH}_3)_2NC_6H_4Hg$

In contrast to this, the spectra of the arylmercury derivatives of quinone phenylhydrazones are similar to the spectra of the corresponding methylphenylhydrazones. Consequently, arylmercury derivatives of this type, like the corresponding unsubstituted compounds, possess a quinonehydrazone structure. To establish the structure of the arylmercury derivatives in the solid state, the IR spectra of their powders were recorded in the region 1500–1700 cm^{-1}; see Fig. 4*.

Fig. 4. IR spectra of powders of arylmercury derivatives:

$A = RHgON=NC_6H_5$;

Fig. 4

Figure 4: Fig. 4

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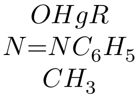
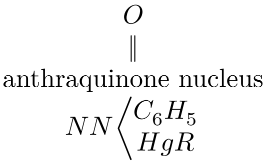
* The absorption spectra were recorded on a spectrovisor in the optical laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR.

$B =$



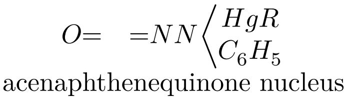
$$\begin{array}{c} OHgR \\ N{=}NC_6H_5 \\ CH_3 \end{array}$$

$V =$



$$\begin{array}{c} O \\ \| \\ \text{anthraquinone nucleus} \\ NN\left\langle\begin{array}{l} C_6H_5 \\ HgR \end{array}\right. \end{array}$$

$G =$



$$\begin{array}{c} O{=}\quad{=}NN\left\langle\begin{array}{l} HgR \\ C_6H_5 \end{array}\right. \\ \text{acenaphthenequinone nucleus} \end{array}$$

where $R = 4\text{-}(\mathrm{CH}_3)_2NC_6H_4-$.

The spectra of the arylmercury derivatives of oxyazo compounds in the region 1580–1700 cm^{-1} have only one intense absorption band at $\sim 1600\ \mathrm{cm}^{-1}$. This same band is also present in the spectra of the corresponding methyl ethers of the oxyazo compounds and is due to vibrations of the $C{=}C$ bonds of the aromatic ring (17). The IR spectra of the arylmercury derivatives of the phenylhydrazones of anthraquinone, acenaphthenequinone, and benzil contain, in addition to the absorption band corresponding to vibrations of the $C{=}C$ bonds, another intense band in the region 1600–

* The IR spectra were recorded on a VIKS-M3 spectrograph in the optical laboratory of the INEOS, Academy of Sciences of the USSR.

1700 cm^{-1}, which is also present in the spectra of unsubstituted compounds and of methylphenylhydrazones of quinones and corresponds to vibrations of the quinoid carbonyl group [18].

Consequently, arylmercury derivatives of oxyazo compounds also have a benzenoid structure in the solid state, whereas derivatives of phenylhydrazones of quinones possess a quinone-hydrazone structure.

Thus, the structure of arylmercury derivatives is fully analogous to that of the unsubstituted compounds and is determined by the relative stability of the benzenoid and quinoid states of the aromatic ring entering into the tautomeric system. The results obtained confirm the earlier conclusion concerning the analogy in the behavior of the arylmercury radical and the hydrogen atom in tautomeric and so-called pseudomeric systems [13–15].

In conclusion, we express our deep gratitude to L. P. Larina and L. P. Volkova for recording the absorption spectra and to N. A. Chumaevskii and E. D. Vlasov for recording the IR spectra.

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