PHENYLMERCURY DERIVATIVES OF AMINOMETHYLENE- AND HYDROXYMETHYLENE-SUBSTITUTED 1-METHYLOXINDOLES, 1-INDANONES, AND 1,3-INDANEDIONES*

Zh. V. Bren', V. A. Bren', L. M. Sitkina,
and V. I. Minkin

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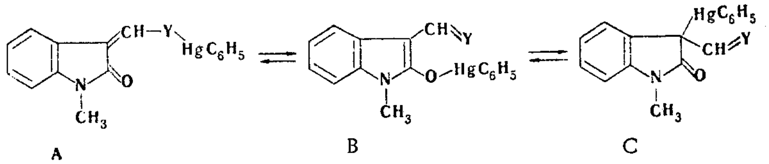
A number of phenylmercury derivatives of 3-hydroxymethylene- and 3-aminomethylene-substituted 1-methyloxindoles, 1-indanones, and 1,3-indanediones were synthesized. It is shown that the preferred tautomeric structures of the potentially metallotropic and prototropic hydroxymethylene keto (hydroxy vinyl aldehyde) derivatives of the indicated compounds and 3-hydroxybenzo[b]-2-formylthiophene coincide precisely. An aminomethylene structure with an N–H bond is realized for the phenylmercury derivatives of the corresponding azomethines in all cases.

We have previously synthesized and investigated organomercury derivatives of N-alkyl- and N-arylamines of 2- and 3-hydroxy(mercapto)benzo[b]-formylfurans and benzo[b]-2-formylthiophenes [2].

The present research was devoted to the synthesis and study of the structures of phenylmercury derivatives of 3-aminomethylene- and 3-hydroxymethylene-1-methyloxindoles (I, II), 2-aminomethylene- and 2-hydroxymethylene-1-indanones (III), and 1,3-indanediones (IV, V). One of the following metallotropic forms or an equilibrium between them in solution are possible for compounds of this type:



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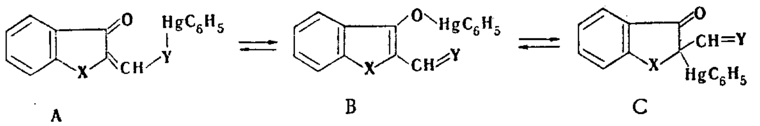

I Y=NAr, NAlk; II Y=O;
III X=CH$_2$, Y=NAr, NAlk; IV, X=CO, Y=NAr, NAlk; V X=CO, Y=O; VI X=S, Y=O

Hydroxymethylene phenylmercury derivatives II, V, and VI were synthesized by two methods: by reaction of the corresponding hydroxymethylene compound or hydroxy aldehyde with phenylmercuric hydroxide (a) or with phenylmercuric acetate (b). The phenylmercury derivatives (I, III, and IV) of the aminomethylene-substituted compounds were also obtained by two methods: a) by reaction of the previously described [1, 3] heterocyclic aminomethylene ketones with phenylmercuric hydroxide and c) by condensation of phenylmercury hydroxymethylene derivatives with amines.

Phenylmercury derivatives II, V, and VI are colorless crystalline substances that are quite soluble in dimethyl sulfoxide (DMSO) and 1-methylpyrrolidone. The phenylmercury derivatives (I, III, and IV) of the aminomethylene-substituted compounds are slightly soluble

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TABLE 1. Phenylmercury Derivatives I-VI

Compound	X	Y	Synthetic method	mp, °C (dec.)	Found, %			Empirical formula	Calc., %		
					C	H	Hg		C	H	Hg
Ia	NCH_3	NC_6H_5	a	128			38,5	$C_{22}H_{18}HgN_2O$			38,3
			c	129			39,0				
Ib	NCH_3	NC_3H_7-*iso*	a	110			39,4	$C_{19}H_{20}HgN_2O$			39,1
II	NCH_3	O	a	135—136	44,7	2,7	46,0	$C_{16}H_{13}HgNO$	44,0	3,0	46,0
			b	135			46,3				
IIIa	CH_2	NC_6H_5	a	154	52,1	2,9	39,5	$C_{22}H_{17}HgNO$	51,6	3.3	40.1
IIIb	CH_2	$NC_6H_4OCH_3$-*p*	a	137—138			37,5	$C_{23}H_{19}HgNO_2$			37,0
IIIc	CH_2	NC_3H_7-*iso*	a	126—127			41,5	$C_{18}H_{19}HgNO$			41,6
IVa	CO	NC_6H_5	a	151			38,1	$C_{22}H_{15}HgNO_2$			37,6
			c	151			37,8				
IVb	CO	$NC_6H_4OCH_3$-*p*	a	209	49,3	2,7	36,8	$C_{23}H_{17}HgNO_3$	49,7	3,1	36,1
			c	208—209			36,2				
IVc	CO	NC_6H_4Cl-*p*	a	224—225	47,8	2,6	35,8	$C_{22}H_{14}ClHgNO_2$	47,2	2,5	36,0
			c	222—223			35,4				36,0
IVd	CO	NC_3H_7-*iso*	a	240			40,8	$C_{19}H_{17}HgNO_2$			40,8
V	CO	O	a	154—155	42,6	2,3	44,0	$C_{16}H_{10}HgO_3$	42,6	2,2	44,4
			b	153			44,3				
VI	S	O	a	138—139	39.9	2,5	44,4	$C_{15}H_{10}HgO_2S$	39,6	2,2	44.1
			b	138—139			44,6				

TABLE 2. Spectral Characteristics of I-VI

Compound in Table 1	UV spectra		IR spectra of mineral oil suspensions, ν, cm^{-1} ($\Delta\nu_{C=O}$)*
	solvent	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	
Ia	DMSO	283 (10,03), 290 (9,77), 380 (19,01)	1605, 1645 (35)
	C_6H_6	292 (14,51), 387 (18,30)	
Ib	DMSO	272 (23,40), 320 (14,25), 347 (14,04)	1560, 1580, 1615, 1645 (25)
	C_6H_6	285 (17,17), 320 (6,37), 365 (15,14)	
II	DMSO	270 (15,11), 325 (13,17)	1610, 1670 (10)
	C_6H_6	315 (11,85), 340 (7,84)	
IIIa	DMSO	390 (29,21)	1610, 1635, 1690 (5)
	C_6H_6	295 (5,92), 395 (24,8)	
IIIb	DMSO	295 (7.07), 395 (27.33)	1605, 1690 (10)
	C_6H_6	303 (5,60), 405 (21,54)	
IIIc	DMSO	285 (2,71), 297 (2.96), 360 (19.23)	1610, 1625, 1655 (35)
	C_6H_6	300 (3,55), 380 (20.27)	
IVa	DMSO	307 (6,71), 375 (27,02)	1590, 1640 (5), 1690 (10)
	C_6H_6	305 (6,37), 370 (24.70)	
IVb	DMSO	293 (6,64), 305 (6.78), 380 (30.37)	1590, 1635 (10), 1690 (10)
	C_6H_6	293 (6,17), 306 (8,15), 375 (25,08)	
IVc	DMSO	295 (7.54), 305 (8,62), 370 (31,5)	1595, 1640, 1695 (5)
	C_6H_6	293 (5,04), 305 (7,81), 370 (26.31)	
IVd	DMSO	286 (8,09), 297 (15.03), 338 (23,83)	1590, 1640 (4), 1685 (12)
	C_6H_6	287 (11,64), 300 (16,36), 340 (17,91)	
V	DMSO	275 (11,12), 287 (18,81), 317 (10,60), 330 (9,89)	1598, 1650 (30), 1700 (22)
	C_6H_6	294 (12,53), 308 (7,75), 320 (9,02)	
VI	DMSO	297 (11,43), 400 (8,41)	1660, 1620, 1638 (−13)
	C_6H_6	318 (10,82), 385 (3,44)	

*This is the $\nu_{C=O,H\ form} - \nu_{C=O,HgPh\ deriv.}$ difference.

yellow or yellow-green crystalline powders (Table 1). The reaction of the phenylmercury derivative (V) of 2-hydroxymethylene-1,3-indanedione with arylamines in benzene or alcohol is accompanied by the formation of intermediate relatively soluble adducts with the composition $V \cdot ArNH_2$, which are unstable and rapidly split out a molecule of water to give stable phenylmercury aminomethylene derivatives of the IV type, which precipitate from the solution in the form of crystals. We preparatively isolated aniline adduct VII, which corresponds to the composition $V \cdot C_6H_5NH_2$ and displays absorption in the IR spectrum in the region of stretching vibrations of the NH_2 group. Treatment of alcohol solutions of II, V, and VI with sodium methoxide causes detachment of a phenylmercury fragment to give the corresponding sodium salts of the starting hydroxy aldehydes.

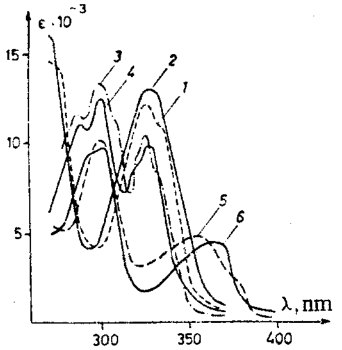

Fig. 1. Electronic absorption spectra in benzene: 1) 1-methyl-3-hydroxymethyleneoxindole; 2) its phenylmercury derivative (II); 3) 2-hydroxymethylene-1,3-indanedione; 4) its phenylmercury derivative (V); 5) 3-hydroxybenzo[b]-2-formylthiophene; 6) its phenylmercury derivative (VI).

The electronic absorption spectra of I-VI (Table 2) contain a band at 330-400 nm, as in the case of the spectra of the corresponding anils and hydroxy aldehydes. The position of this band is virtually independent of the polarity of the solvent and a change in the temperature in each individual type of compound. This constitutes evidence for the existence of their molecules in one of three forms (A, B, and C). The position of the absorption bands in the vibrational spectra of all of the investigated organomercury compounds does not exceed 1700 cm^{-1} (Table 2). Consequently, form C can be excluded from consideration, since the band of the carbonyl absorption for C-mercurated tautomers C should be found at 1720-1750 cm^{-1}.

The aldehydes of 1,3-indanedione and 1-methyloxindole exist in hydroxymethylene form A [4, 5], while hydroxy aldehyde structure (type B) corresponds to 3-hydroxybenzo[b]-2-formylthiophene [6].

An analysis of the electronic and vibrational spectra of the mercurated hydroxy aldehyde derivatives shows that the structure of the phenylmercury compounds coincides precisely with the preferred tautomeric structure of the aldehydes.

The almost completely identical character of their electronic absorption spectra (Fig. 1) serves as evidence in favor of this. The degree of coordination of the mercury atom with the carbonyl oxygen atom in the II, V, and VI molecules can be judged from the change in the carbonyl absorption frequency ($\Delta\nu_{C=O}$) as compared with the starting hydroxy aldehydes, in which there is an intramolecular hydrogen bond (Table 2). The large decrease in the frequency of the stretching vibrations of the carbonyl group in phenylmercury derivatives II and V constitutes evidence for strong intramolecular PhHg...O=C$<$coordination. This effect is absent in the case of aldehyde VI. The absorption of the aldehyde group here has a higher frequency than in the case of hydroxy- and even 3-methoxybenzo[b]-2-formylthiophene [6]. A comparison of the electronic absorption spectra of phenylmercury derivatives I, III, and IV in various solvents (Table 2) with the spectra of the starting aminomethylenes [1, 3] also reveals their completely identical character, and this may serve as evidence for the existence in solution of all three compounds I, III, and IV in the A form. This conclusion is in agreement with the results of a study of the structures of phenylmercury compounds with a similar potentially tautomeric fragment. It must be noted that monotypically constructed N-phenylmercury aminomethylene compounds are formed from aldehydes II, V, and VI, which have different types of tautomeric fragments, on reaction with amines.

The IR spectral data confirm the keto amine structure of the mercury derivatives. The character of the bands at 1600-1700 cm^{-1} corresponds to form A, and absorption is absent in the region of the frequencies of the vibrations of the OH and NH bonds. A long-wave shift of the frequencies of the absorption of the carbonyl groups as compared with the starting NH compounds is noted for all of the compounds, and this constitutes evidence for the existence of coordination of the mercury atom with the carbonyl oxygen atom. Judging from the $\Delta\nu_{C=O}$ value (Table 2) the most pronounced changes in the coordination on passing from the amino (NH) to the phenylmercury (NHgPh) molecules are observed for the compounds that have a weak hydrogen bond in the NH form (types I and III).

Thus, in contrast to aldehydes II, V, and VI, variation of the structure of the radical of the amine component and of the annelated (to the potentially tautomeric fragment) portion of molecules of the I, III, and IV type does not affect the position of equilibrium (1): in all cases the mercury atom is bonded to a "soft" center — the nitrogen atom.

EXPERIMENTAL

The absorption spectra of the compounds in the UV and visible regions were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions and carbon tetrachloride solutions of the compounds were obtained with a UR-20 spectrometer. The PMR spectra were recorded with a Tesla BS-407-C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

Synthesis of the Phenylmercury Derivatives. A) A suspension of 0.011 mole of phenylmercuric hydroxide was added to an alcohol solution of 0.01 mole of the hydroxy aldehyde or aminomethylene ketone, and the solution was heated on a water bath for 5-10 min and cooled. The resulting precipitate was recrystallized from a suitable solvent to give the product in 60-80% yield. PMR spectrum of V (in 1-methylpyrrolidone), δ: CH 8.82 (s), H_{arom} 7.0-7.8 ppm (m). IR spectrum of V (in CCl_4), ν: 1515, 1553, 1580, 1630, and 1686 cm^{-1}. PMR spectrum of VI, δ: CH 9.87 (s), H_{arom} 7.0-8.1 ppm (m).

B) A 0.01-mole sample of the hydroxy aldehyde was added to an alcohol solution of 0.011 mole of phenylmercuric acetate, and the mixture was heated at 50°C for 10 min. It was then cooled, and the precipitated colorless acicular crystals were recrystallized from absolute benzene. The V and VI derivatives obtained by methods A and B were identical (Table 1).

C) A 0.0051-mole sample of the corresponding arylamine was added to a suspension of 0.005 mole of phenylmercury-substituted aldehydes V or VI in 5 ml of methanol, and the resulting clear yellow-green solution was heated briefly. It was then cooled, as a result of which crystals of the phenylmercury aminomethylene derivative began to precipitate. The products were obtained in 70-80% yields.

Adduct VII. A 0.005-mole sample of the phenylmercury derivative (V) of 2-hydroxymethylene-1,3-indanedione was suspended in 5 ml of methanol, 0.005 mole of aniline was added, and the mixture was heated on a water bath for 1 min, as a result of which the solution became clear. Rapid cooling precipitated yellow-green needles, which were removed by filtration and washed with cold pentane to give a product with mp 112-113°C (dec.). IR spectrum, ν: 1544, 1593, 1640, 1690, and 3450 cm^{-1}. Found: C 48.53; H 3.14%. $C_{22}H_{17}HgNO_3$. Calculated: C 48.56; H 3.34%.

Crystals of mercury derivative IVa precipitated when an alcohol or benzene solution of VII was heated on a water bath for 10 min.

The compounds were analyzed for their mercury content by a volumetric method [7].

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