BENZOID–QUINOID TAUTOMERISM OF AZOMETHINES AND THEIR STRUCTURAL ANALOGS

XXIII.* MERCURY DERIVATIVES OF ANILS OF o-HYDROXY AND o-MERCAPTO ALDEHYDES OF THE BENZO[b]THIOPHENE AND BENZO[b]FURAN SERIES

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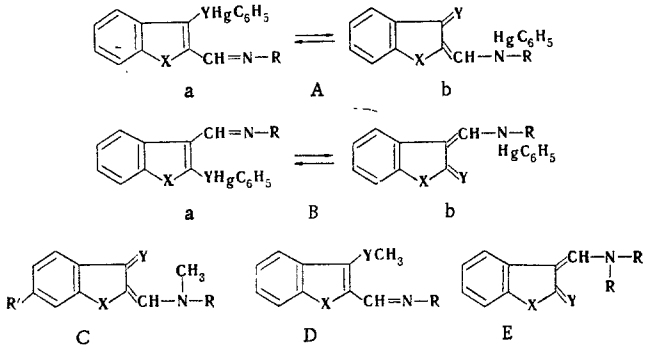
A number of organomercury derivatives of N-alkyl- and N-arylimines of 2- and 3-hydroxy-(mercapto)formylbenzo[b]furans and 2- and 3-hydroxy(mercapto)formylbenzo[b]thiophenes were synthesized. A conclusion regarding the position of the C_6H_5Hg group in these compounds was drawn from the vibrational and electronic absorption spectra.

Metallotropic tautomerism in organomercury and organothallium derivatives of aromatic hydroxy aldehydes and their imines was proved by electronic spectroscopy and luminescence methods. However, data on the possibilities of metallotropic transformations in organomercury derivatives of o-hydroxy and o-mercapto aldimines of the heteroaromatic series are not available.

The present research is devoted to a study of the capacity of organomercury derivatives of the benzo-[b]thiophene and benzo[b]furan series for intra- or intermolecular metallotropic rearrangements and to the clarification of the effect of replacement of a proton by an organometallic residue on the relative stabilities of the benzoid and quinoid forms.

We obtained phenylmercury derivatives of the A and B type and studied their electronic and vibrational spectra.



X = O, S; Y = O, S; R = Ar, Alk; R' = H, CH_3

The characteristics of the synthesized compounds and the R values are presented in Table 1.

The absorption spectra of compounds A and B (Y = O) contain a band at 400-460 nm, just as in the spectra of the corresponding anils, which have ketone–amine structures C and E (Y = O) [2] (Fig. 1 and

*See [1] for communication XXII.

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TABLE 1. Compounds A and B

Type of compound	Compound No.	Compound X	Y	R	R′	mp, °C	Empirical formula	Hg, % found	Hg, % calc.	Yield, %
A	I	S	O	C_6H_5	H	162—163	$C_{21}H_{15}NOSHg$	37,6	37,9	71
A	II	S	O	p-$CH_3OC_6H_4$	H	187	$C_{22}H_{17}NO_2SHg$	35,6	35,8	63
A	III	S	O	p-BrC_6H_4	H	208—209	$C_{21}H_{14}NOSHgBr$	33,2	32,9	68
A	IV	S	O	$CH_2C_6H_5$	H	144—145	$C_{22}H_{17}NOSHg$	36,6	36,9	58
A	V	O	O	C_6H_5	H	132—133	$C_{21}H_{15}NO_2Hg$	38,8	39,0	79
A	VI	O	O	p-ClC_6H_4	H	175	$C_{21}H_{14}NO_2HgCl$	36,0	36,2	69
A	VII	O	O	C_6H_5	CH_3	195	$C_{22}H_{17}NO_2Hg$	36,8	37,2	81
A	VIII	O	O	p-$CH_3OC_6H_4$	CH_3	162—163	$C_{23}H_{19}NO_3Hg$	36,1	36,0	74
A	IX	O	O	p-$NO_2C_6H_4$	CH_3	173—174	$C_{22}H_{16}N_2O_4Hg$	34,7	35,0	62
A	X	S	S	C_6H_5	H	177—178	$C_{21}H_{15}NS_2Hg$	36,4	36,7	60
A	XI	S	S	p-$CH_3C_6H_4$	H	166	$C_{22}H_{17}NS_2Hg$	36,3	35,8	53
A	XII	S	S	p-$CH_3OC_6H_4$	H	138	$C_{22}H_{17}NOS_2Hg$	34,5	34,8	60
A	XIII	S	S	p-ClC_6H_4	H	178	$C_{21}H_{14}NS_2HgCl$	34,2	34,6	66
A	XIV	S	S	CH_3	H	182	$C_{16}H_{12}NS_2Hg$	41,0	41,4	80
A	XV	S	S	C_4H_9	H	132	$C_{19}H_{19}NS_2Hg$	37,8	38,1	78
A	XVI	O	S	C_6H_5	H	110	$C_{21}H_{15}NOSHg$	37,5	37,9	68
A	XVII	O	S	p-$CH_3C_6H_4$	H	132	$C_{22}H_{17}NOSHg$	36,8	36,9	75
A	XVIII	O	S	p-$CH_3OC_6H_4$	H	165	$C_{22}H_{17}NO_2SHg$	35,6	35,8	70
A	XIX	O	S	p-ClC_6H_4	H	155	$C_{21}H_{14}NOSHgCl$	35,3	35,5	85
A	XX	O	S	$CH_2C_6H_5$	H	125	$C_{22}H_{17}NOSHg$	36,6	36,9	61
B	XXI	S	O	C_6H_5	H	210	$C_{21}H_{15}NOSHg$	37,8	37,9	67
B	XXII	S	O	p-$CH_3COC_6H_4$	H	238	$C_{23}H_{17}NO_2SHg$	34,8	35,1	70
B	XXIII	S	O	p-$CH_3OC_6H_4$	H	186—187	$C_{22}H_{17}NO_2SHg$	36,0	35,8	64
B	XXIV	S	O	$CH_2C_6H_5$	H	177—178	$C_{22}H_{17}NOSHg$	36,8	36,9	78

TABLE 2. Spectral Characteristics of Compounds A and B

Compound No. from Table 1	UV spectra: solvent	UV spectra: λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	IR spectra in mineral oil, ν, cm^{-1}
I	DMF	330 (14,3); 445 (21,7)	1590, 1625
	Benzene	335 (16,4); 460 (20,7)	
II	DMF	340 (15,0); 460 (18,9)	1590, 1640
III	DMF	338 (14,5); 460 (19,0)	1585, 1610
IV	DMF	328 (10,1); 435 (15,8)	1595, 1615
V	DMF	315 (9,6); 420 (16,7)	1590, 1635
	Benzene	330 (8,2); 435 (16,7)	
VI	DMSO	322 (9,4); 420 (25,2)	1590, 1640
	Benzene	328 (6,3); 430 (21,8)	
VII	DMF	330 (11,9); 410 (28,8)	1585, 1635
	Benzene	328 (9,8); 418 (24,3)	
	Acetone	320 (9,4); 405 (20,2)	
	Methanol	335 (11,6); 417 (33,5)	
VIII	Benzene	330 (10.9); 446 (18,8)	1585, 1640
IX	Benzene	345 (22,8); 440 (29,0); 460 (29,1)	1590, 1625, 1645
X	DMF	370 (18,2)	1580, 1610
	Benzene	368 (16,3)	
XI	DMSO	372 (20.7)	1560, 1600
XII	DMSO	375 (22,8); 390 (22,8)	1580, 1610
XIII	Benzene	370 (17,4)	1580, 1605
XIV	DMSO	312 (13,8); 355 (9,2)	1625
	Benzene	318 (11,4); 365 (5,6)	
XV	DMSO	314 (13,2); 355 (8,9)	1625
	Benzene	318 (11,4); 360 (5,9)	
XVI	DMSO	322 (12,7); 380 (12,5)	1580, 1620
	Benzene	327 (18,6); 402 (16,1)	
XVII	DMSO	325 (21,5); 405 (21,3)	1595, 1635
XVIII	DMSO	330 (22,4); 432 (22,3)	1580, 1615
XIX	DMSO	325 (16,0); 388 (16,0)	1570, 1605
	Benzene	328 (19,4); 403 (19,0)	
XX	DMSO	315 (19,3); 322 (18,7); 380 (11,3)	1635
XXI	DMSO	270 (20,3); 395 (40,3)	1590, 1610
	Benzene	278 (23,1); 400 (38,1)	
XXII	DMSO	288 (21,7); 415 (54,4)	1600, 1660
	Benzene	288 (17,5); 415 (49,6)	
XXIII	DMSO	275 (11,4); 305 (7,9); 395 (22,8)	1605
	Benzene	280 (14,8); — 410 (19,7)	
XXIV	DMSO	275 (14,9); 365 (13,5)	1590, 1605
	Benzene	282 (13,8); 380 (13,0)	

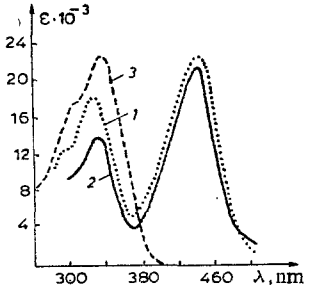

Fig. 1

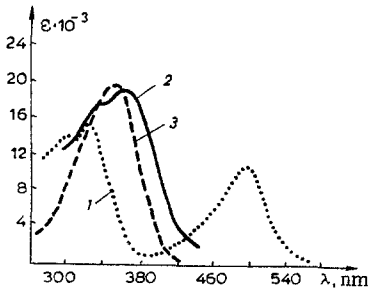

Fig. 2

Fig. 1. Electronic absorption spectra (in dimethylformamide): 1) 2-(N,N-methylphenylaminomethylene)-3(2H)-benzothiophenone; 2) phenylmercury derivative of the anil of 2-formyl-3-hydroxybenzo[b]-thiophene; 3) anil of 2-formyl-3-methoxybenzo[b]thiophene.

Fig. 2. Electronic absorption spectra (in dimethylformamide): 1) 2-(N,N-dimethylaminomethylene)-3(2H)-benzothiophenethione; 2) phenylmercury derivative of the anil of 2-formyl-3-mercaptobenzo-[b]thiophene; 3) anil of 2-formyl-3-methylmercaptobenzo[b]thiophene.

Table 2). The polarity of the solvent, the character of the substituent in the benzene ring, and a change in the temperature have practically no effect on the position of this band. This indicates coordination of the C_6H_5Hg group at the nitrogen atom and the existence of compounds A and B (Y=O) in the quinoid form (b).

The stretching vibrations of a conjugated carbonyl group appear in the IR spectra of the compounds under discussion at lower frequencies (1600-1645 cm^{-1}) than in the spectra of the corresponding unsubstituted anils C (1655-1715 cm^{-1}) (Table 2). This constitutes evidence for additional intramolecular coordination of the carbonyl oxygen atoms with mercury and a chelate structure for compounds A and B. A decrease in the double bond character of the C=O group was also observed in the vibrational spectra of N-phenylmercury derivatives of 3,5-dichloro-2-pyridone [3] and received a similar explanation.

The electronic absorption spectra of compounds A (Y=S) differ substantially from the spectra of the corresponding anils C (Y=S) [4] (Fig. 2). The insensitivity of the position and the intensity of the band at 320-370 nm to the polarity of the solvent and the character of R (Table 2) makes it possible to conclude that the mercury derivatives under discussion have a benzoid structure (a) and that exchange of the phenylmercury residue between the sulfur and nitrogen atoms is absent.

The IR spectroscopic data confirm the conclusion regarding the imine structure (a) of compounds A (Y=S). The spectra contain bands at 1605-1635 cm^{-1} (Table 2), which we assigned to the stretching vibrations of the C=N group; this corresponds to the vibrations of this bond in compounds of the D type [4] with a fixed benzoid structure.

The results are in agreement with the known tendency of the mercury atom to form a bond with the sulfur atom in sulfur-containing ligands and to the preferred bonding with the softer nitrogen centers in bidentate ligands containing nucleophilic nitrogen and oxygen atoms [5].

EXPERIMENTAL METHOD

Phenylmercury derivatives A and B were obtained by refluxing equimolecular amounts of phenylmercury hydroxide and the appropriate anil in ethanol or propanol for 5-10 min and subsequent crystallization from isopropyl alcohol. The compounds are powdery substances that are only slightly soluble in ordinary organic solvents.

The absorption spectra were recorded with a Specord UV-Vis recording spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer.

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