

## Mercuration of Schiff bases of thiosubstituted benzylidene anilines

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The mercuration of thiosubstituted benzylidene anilines **3/4** derived by condensing corresponding amines **1** or **2** with *para*-substituted benzaldehydes has been studied. The structural characterisation of the products by IR and <sup>1</sup>H NMR indicates that the mercury is directed to the *para*-position of the N-phenyl ring.

The C-H bond activation via metal catalysed route is a topic of current interests that could lead to new functionalisation at carbon centre<sup>1-12</sup>. The process is more extensive in case of transition metal chemistry<sup>1,3-7</sup> than nontransition metals<sup>2,8-13</sup>. Recently the organic chemistry of mercury<sup>2a</sup> and its biochemical and organometallic applications<sup>7-13</sup> have attracted special attention. The use of organomercurials in the synthesis of M-C  $\sigma$ -bonded organometallics has several advantages<sup>11-13</sup> over the classical organolithium and Grignard reagents; the main are transmetallation reaction<sup>11</sup> to prepare different other organometallics those are otherwise difficult or could not be obtained and easy to handle in air and moisture compared to other synthetic precursors. The sites of mercuration of aromatics are electron population controlled and the stability of the products arise from the conformation of the substrate<sup>9,12</sup>. We reported earlier the monomercuration of thioazomethines<sup>12</sup>. Herein we report the regioselective dimercuration of 1, 2-bis[2-thio-(N-benzylidene)anilines]ethane **3** and 1,3-bis[2-{thio-(N-benzylidene)}anilines]propane **4**.

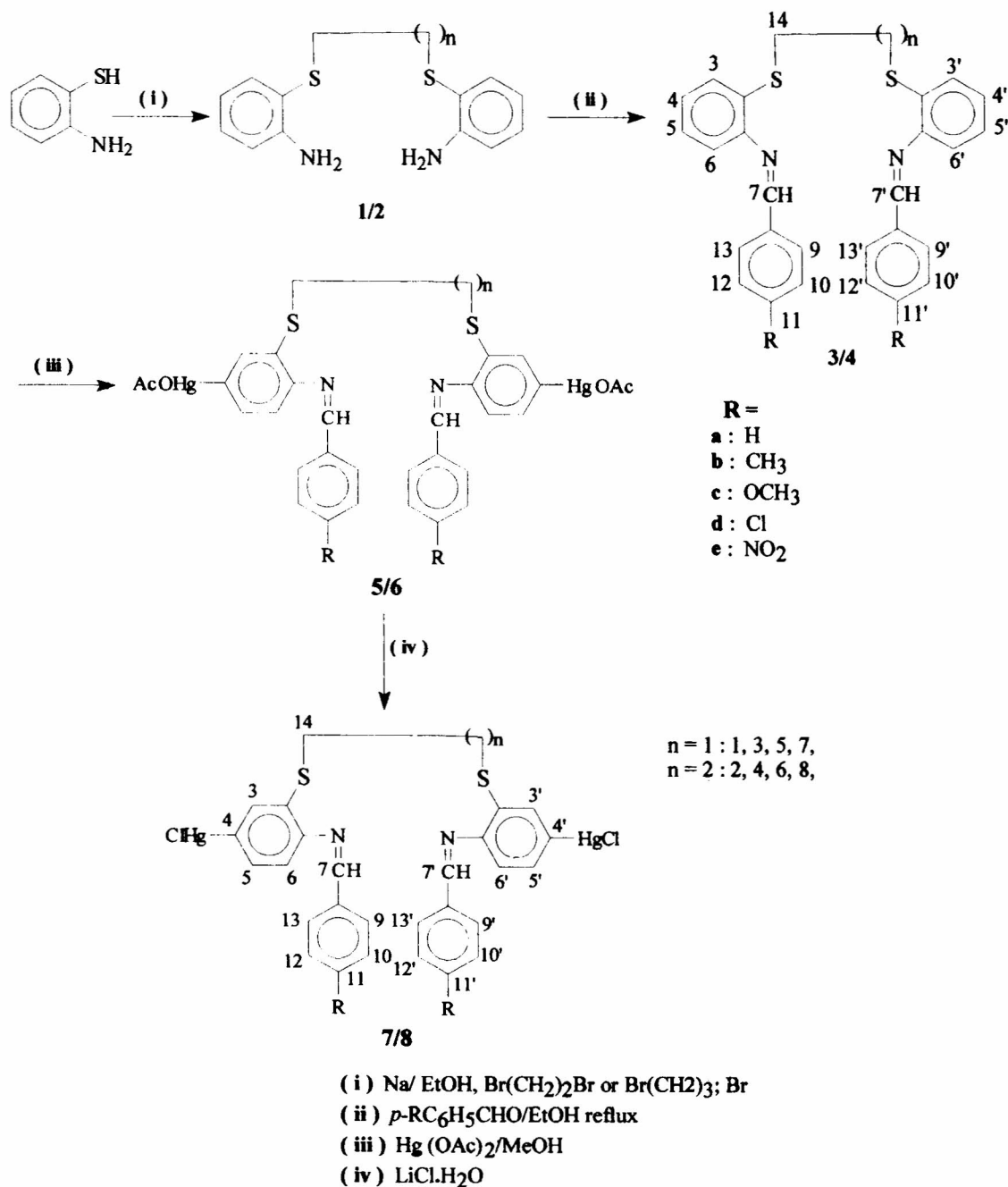
The Schiff bases and organomercurials described in this work are shown in Scheme I along with the reagents and conditions used for synthesis. The chloromercurio derivatives **7/8** of azomethines were prepared by reacting Hg(OAc)<sub>2</sub> with the ligands in 1:2 mole ratio followed by the addition of LiCl. The acetato complexes **5/6** were also isolated from the solution before adding LiCl but not studied critically.

The appearance of sharp strong stretch in IR

spectra at 1600-1625 cm<sup>-1</sup> in ligands **3/4** is suggestive of  $\nu(\text{C}=\text{N})$  mode<sup>14</sup>. In complexes the position remains almost unshifted and is an indication of free azomethine group. The complexes **7/8** exhibit a sharp single stretch at 325-335 cm<sup>-1</sup> due to  $\nu(\text{Hg}-\text{Cl})$ . The  $\nu(-\text{S}-\text{CH}_2-)$  mode of the free ligands **3/4** appear as a split band at 680-690 and 645-655 cm<sup>-1</sup> and  $\nu(\text{C}-\text{S})$  exhibits the stretching mode at 755-780 cm<sup>-1</sup><sup>15</sup>. These bands in complexes remain undisturbed and the absence of  $\nu(\text{Hg}-\text{S})$  suggest noncoordination of thioether group<sup>16</sup>. The acetato complexes **5/6** exhibit strong bands  $\nu_{\text{as}}(\text{COO})$  at 1525-1540 and  $\nu_{\text{s}}(\text{COO})$  at 1300-1320 cm<sup>-1</sup> ( $\Delta\nu = 220-225$  cm<sup>-1</sup>) correspond to unidentate character of bonded -COO group<sup>14</sup>.

The complexes are sparingly soluble in common organic solvents and the UV-Vis spectra are recorded in DMSO. The bands at 345-380 nm and 280-295 nm in ligands may be ascribed to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  charge transfer transitions respectively<sup>16</sup> and in complexes the positions are blue shifted by 15-25 nm.

The site of mercuration is estimated from the <sup>1</sup>H NMR spectral studies. All aromatic protons of the ligands **3/4** and mercurated derivatives **7/8** are unambiguously assigned on the basis of spin-spin structure and changes therein on substitution. The spectra of ligands in CDCl<sub>3</sub> and the complexes in DMSO-*d*<sub>6</sub> are in complete agreement with the structures in which the halves of the molecule are magnetically equivalent to each other (e.g. 6 = 6' etc.). The aromatic region for **3b-c**, **4b-e**, **7b-e** and **8b-e** displays a group of left



Scheme I

right symmetrical multiplet peaks characterising the four spin AA'BB' system : 9-(9'-)H, 13-(13'-)H for 3/4 at 7.4-8.0 and 7/8 at 7.8-8.1, 10, (10'-)H, 12-(12'-)H for 3/4 at 7.2-8.1 and 7/8 at 7.2-8.2 ppm. The signals due to 10-(10'-) and 12-(12'-)H vary considerably with different substituents R in the aromatic aldehyde. The signal movement is in accord with the inductive and resonance effect of the group R. Due to the methyl substitution in 3b,

4b, 7b and 8b the signal suffers upfield shifting. The maximum upfield shifting as expected is observed in methoxy derivatives for 10-(10'-) and 12-(12'-)H as *ortho*-position is directly participated in the T effect<sup>12(b)</sup>. The reverse effect is seen in 3e or 4e and 7e or 8e. The electron withdrawing character of -NO<sub>2</sub> shifts the signals considerably downfield, so these can only be assigned to the C-phenyl protons.

The signals at higher field correspond to N-phenyl protons and the field position is explained based on the high electron density in the N-phenyl ring<sup>17</sup>. They remain almost unperturbed on substitution in C-phenyl ring. The imine proton (7-H) is expectedly appear at the most downfield position as a sharp singlet and moves slightly on either direction depending on the nature of substituents R. The aliphatic protons are expectedly at higher field; 14, 14'-H appear as triplet and 15-H (for **4a-e** and **8a-e** only) appear as quintet protons.

The zonal differences in spectral pattern and field position are observed in chloromercuriated derivatives **7/8** in comparison to the ligands **3/4**. The N-phenyl protons are severely affected. The most significant feature is the loss of resonance due to 4-(4'-)H of the N-phenyl ring from the NMR spectra and the appearance of new singlet due to 3-(3'-)H at very downfield position, 5-(5'-)H signals are downfield shifted in complexes **7/8** by about  $\sim 0.2$  ppm compared to the free ligand values **3/4**, 3-(3'-)H signals in complexes **7/8** are slightly at upfield position ( $\sim 0.1$  ppm) relative to 5-(5'-)H signals may be due to electron releasing effect of  $-S-CH_2-(CH_2)_n$  ( $n=1/2$ ) group. There are two AB type doublets 5-(5'-) and 6-(6'-)H which suffer downfield shift in complexes compared to free ligands and do not vary significantly with substituents R in the C-phenyl ring. The protons 9-(9'-) to 13-(13'-)H at C-phenyl ring suffer insignificant change on complexation. This clearly shows mercury is directed selectively to the *para*-position of the N-phenyl ring rather than *ortho*-position of the C-phenyl ring which is the usual position for cyclopalladation reaction<sup>1,4</sup>. The sulfur coordination is also excluded as the  $-S-CH_2-$  signals remain unaffected<sup>12b</sup> on mercuriation. The azomethine proton signal is also insignificantly affected in complexes and supports the N-phenyl mercuriation. A representative spectra of ligand **4d** and complex **8d** are shown in Figure 1 and data are collected in Table I.

The regioselective mercuriation is justified on the basis of electron density distribution and the stability of the product is conformation controlled<sup>9,12b</sup>. The upfield position of the N-phenyl protons indicative higher electron density of the ring relative to C-phenyl ring. This accounts the  $\pi$ -complex formation of N-phenyl ring with electrophile  $Hg(OAc)^+$ . The conformational stability of thioazomethine directs  $Hg(OAc)^+$  to *para*-position of the N-phenyl ring and hence the regioselectivity.

## Experimental Section

The solvents used in the reactions were of reagent grade and were dried by reported procedures<sup>18</sup>.  $Hg(OAc)_2$  was purchased from Loba Chemie Indo Australanal Co., Bombay. All other chemicals were reagent grade and were used as received. IR spectra (KBr) were recorded on a Perkin-Elmer 783 and 883 spectrophotometer, <sup>1</sup>H NMR spectra on a varian XL 200 and Bruker 300 MHz FT NMR spectrometers in  $CDCl_3$  for **3/4** and in  $DMSO-d_6$  for **7/8** using TMS as internal standard and UV-Vis spectra on a Shimadzu UV 160A spectrometer. Elemental analyses were obtained by using a Perkin-Elmer 240C elemental analyser.

**1, 2-Bis[2-thio(N-benzylidene)aniline]ethane 3a.** Benzaldehyde (1.54 g, 14.50 m moles) was added to dry ethanolic solution (20 mL) of 1, 2-Bis[(2-aminophenyl)thio]ethane **1**<sup>19</sup> (2 g, 7.25 m moles) and refluxed for 2 hr on a steam bath. The orange yellow solution was cooled to room temperature when dark coloured gummy mass separated slowly. The light yellow supernatant liquid was decanted off. The mass was further boiled with dry ethanol on a steam bath, cooled and supernatant liquid was decanted off twice as earlier. It was evaporated under reduced pressure and dried over  $CaCl_2$ . The yield was low, 30%. Other schiff bases were prepared similarly and the yield varied in the range of 30-50%.

1, 3-Bis[(2-aminophenyl)thio]propane **2** was also synthesised by reported procedure<sup>19</sup> and it was used to prepare 1, 3-bis[2-thio(N-benzylidene)aniline]propane **4**. The compounds **3a** and **4a** yield gummy mass. The solid products obtained from **3b-3e** and **4b-4e** were purified by recrystallization from  $CHCl_3$ -EtOH (1:4 v/v). Melting points are: **3b**,  $52 \pm 1$ ; **3c**,  $120 \pm 1$ ; **3d**,  $135 \pm 1$ ; **3e**,  $170 \pm 1$ ; **4b**,  $44 \pm 1$ ; **4c**,  $85 \pm 1$ ; **4d**,  $96 \pm 1$  and **4e**,  $138 \pm 1^\circ C$ .

**1, 2-Bis[2-thio(4-chloromercurio) (N-benzylidene)aniline]ethane 7a.** A solution of  $Hg(OAc)_2$  (0.35 g, 1.1 m moles) in dry MeOH (20 mL) was added dropwise to a solution of ligand **3a** (0.25 g, 0.55 m moles) in the same solvent (20 mL). The mixture was stirred at controlled temp. within  $15-20^\circ C$  for 48 hr. Very faint precipitate appeared and it was filtered off (warming at this stage yielded acetato derivatives **5/6**).  $LiCl$  (5 m moles) was added to the filtrate in MeOH and the resulting thick mixture was filtered, washed with ether and dried *in vacuo*. The product was recrystallised from  $DMSO$ -MeOH mixture, yield 40%.

Table I—Elemental analysis, IR and <sup>1</sup>H NMR spectral data

Compd	Found (%) (Calcd)			IR (cm <sup>-1</sup> )			<sup>1</sup> H NMR (δ, ppm) J(Hz)							R	
	C	H	N	ν(C=N)	ν(C-S)	ν(Hg-Cl)	3-(3'-)H	4-(4'-)H	5-(5'-)H	6-(6'-)H <sup>c</sup>	7-(7'-)H <sup>c</sup>	9-(9'-) <sup>e</sup> 13-(13'-)H	10-(10'-) 12-(12'-)H		14-(14'-)- <sup>d</sup> H
3a <sup>a</sup>				1620	765		6.70(d)	7.01(t)	7.01(t)	7.21	8.31	7.82	7.62(t) <sup>g</sup>	3.02	
							(8.0)	(9.0)	(9.0)	(8.0)		(8.0)	(9.0)		
3b	74.9	5.6	6.0	1620	755		6.71(d)	7.01(t)	7.01(t)	7.20	8.27	7.78	7.42(d)	3.03	2.38
	(75.0)	(5.8)	(5.8)				(8.0)	(9.0)	(9.0)	(8.0)		(9.0)	(9.0)		
3c	70.0	5.6	5.3	1605	770		6.67(d)	6.95(t)	6.95(t)	7.18	8.26	7.85	7.25(d)	3.09	3.85
	(70.3)	(5.5)	(5.5)				(8.0)	(9.0)	(9.0)	(8.0)		(9.0)	(9.0)		
3d	64.4	4.1	5.3	1620	780		6.73(d)	7.04(t)	7.04(t)	7.27	8.32	7.92	7.69(d)	3.06	
	(64.5)	(4.2)	(5.4)				(8.0)	(9.0)	(9.0)	(8.0)		(8.0)	(9.0)		
3e	61.8	3.9	10.4	1625	780		6.79(d)	7.08(t)	7.08(t)	7.32	8.48	8.05	8.24(d)	3.08	
	(62.0)	(4.1)	(10.3)				(8.0)	(9.0)	(9.0)	(8.0)		(8.0)	(9.0)		
4a <sup>a</sup>				1610	755		6.66(d)	7.02(t)	7.02(t)	7.14 <sup>g</sup>	8.29	7.90	7.58(t) <sup>g</sup>	3.05	2.00
							(8.0)	(9.0)	(9.0)	(8.0)		(8.0)	(9.0)		
4b	75.1	6.2	5.4	1625	765		6.69(d)	7.00(t)	7.00(t)	7.16	8.25	7.75	7.36(d)	3.06	2.04
	(75.3)	(6.1)	(5.7)				(8.0)	(9.0)	(9.0)	(8.0)		(9.0)	(9.0)		
4c	70.6	5.6	5.5	1610	770		6.67(d)	6.96(t)	6.96(t)	7.13	8.29	7.88	7.20(d)	3.08	2.03
	(70.7)	(5.7)	(5.3)				(8.0)	(9.0)	(9.0)	(9.0)		(9.0)	(9.0)		
4d	65.2	4.3	5.2	1615	775		6.71(d)	7.06(t)	7.06(t)	7.18	8.32	7.94	7.58(d)	3.09	2.05
	(65.0)	(4.5)	(5.2)				(8.0)	(9.0)	(9.0)	(8.0)		(9.0)	(9.0)		
4e <sup>b</sup>	62.4	4.4	10.2	1630	775		6.75(d)	7.09(t)	7.09(t)	7.22	8.46	8.08	8.24(d)	3.10	2.05
	(62.5)	(4.3)	(10.1)				(8.0)	(9.0)	(9.0)	(8.0)					
7a	36.5	2.2	3.2	1622	765	330	7.44(s)		7.37(d)	7.32	8.38	7.89	7.69(t) <sup>g</sup>	3.05	
	(36.4)	(2.4)	(3.0)						(8.0)	(8.0)		(9.0)	(9.0)		
7b	37.7	2.6	3.1	1625	752	325	7.45(s)		7.35(d)	7.31	8.34	7.84	7.44(d)	3.06	2.40
	(37.9)	(2.7)	(3.0)						(8.0)	(8.0)		(9.0)	(9.0)		
7c	36.5	2.5	3.0	1605	765	328	7.42(s)		7.30(d)	7.27	8.32	7.87	7.27(d)	3.04	3.86
	(36.7)	(2.0)	(2.8)					(8.0)	(8.0)	(9.0)		(9.0)	(9.0)		
7d	34.1	2.1	2.8	1618	783	330	7.46(s)		7.40(d)	7.36	8.42	7.95	7.70(d)	3.07	
	(33.9)	(2.0)	(2.8)						(8.0)	(8.0)		(9.0)	(9.0)		
7e <sup>b</sup>	33.1	2.1	5.6	1628	778	335	7.54(s)		7.49(d)	7.43	8.34	8.07	8.26(d)	3.09	
	(33.2)	(2.0)	(5.5)						(8.0)	(8.0)		(9.0)	(9.0)		
8a	37.3	2.4	3.1	1610	750	330	7.30(s)		7.29(d)	7.23	8.34	7.93	7.62(t) <sup>g</sup>	3.09	2.05
	(37.2)	(2.6)	(3.0)						(8.0)	(8.0)		(9.0)	(9.0)		
8b	38.7	2.8	3.0	1628	765	325	7.33(s)		7.27(d)	7.22	8.33	7.80	7.40(d)	3.10	2.07
	(38.6)	(2.9)	(2.9)						(8.0)	(8.0)		(9.0)	(9.0)		
8c	37.2	3.0	2.9	1607	765	328	7.27(s)		7.24(d)	7.19	8.35	7.90	7.25(d)	3.11	2.09
	(37.3)	(2.8)	(2.8)						(8.0)	(8.0)		(9.0)	(9.0)		
8d	34.5	2.3	2.9	1618	770	330	7.35(s)		7.33(d)	7.27	8.36	7.95	7.64(d)	3.13	2.10
	(34.6)	(2.2)	(2.8)						(8.0)	(8.0)		(9.0)	(9.0)		
8e <sup>b</sup>	34.1	2.3	5.3	1635	770	335	7.44(s)		7.38(d)	7.34	8.51	8.11	8.27(d)	3.15	2.11
	(33.9)	(2.1)	(5.6)						(8.0)	(8.0)		(9.0)	(9.0)		

<sup>a</sup> Gummy mass; <sup>b</sup> ν(NO<sub>2</sub>); 1340-1345 cm<sup>-1</sup>; <sup>c</sup> Doublet; <sup>d</sup> Triplet; <sup>e</sup>

<sup>f</sup> Singlet; <sup>g</sup> Quintet; <sup>h</sup> 11-H appears at the same position

Other complexes **7b-e** were also prepared similarly with yield in the range of 40-60%. The complexes **8** were prepared following identical procedure from the ligands **4** with yield in the range of 30-60%.

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