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Regioselective mercuration of 2-(benzylthio)-*N*-(benzylidene)anilines

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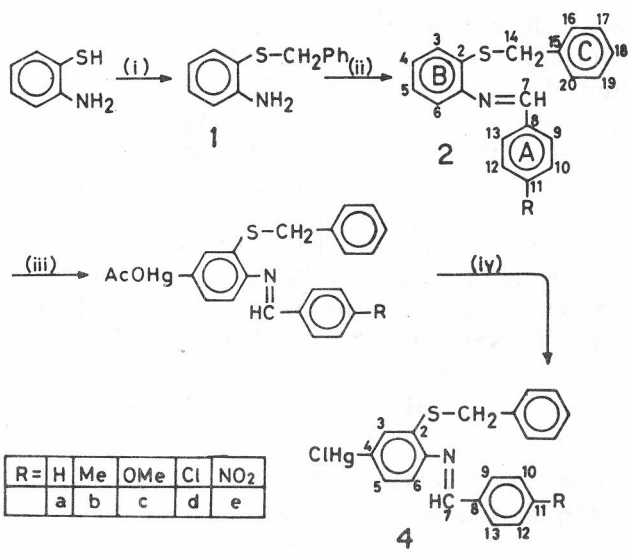
Mercuration of 2-(benzylthio)-*N*-(benzylidene)anilines **2**, derived by the condensation of 2-(benzylthio)aniline **1** with *para*-substituted bennzaldehydes, has been studied. Spectral (IR and ^{1}H NMR) data of the products indicate that mercury is directed to the *para*-position of the *N*-phenyl ring.

Metal mediated C−H bond activation process is a topic of current interest[1] and numerous relevant organometallics have been synthesized and some have been found to be useful in organic syntheses[2]. Organonontransition compounds are relatively less familiar than organotransition compounds probably due to their weak coordinating ability[3]. Recently the organic chemistry of mercury has attracted a great attention[4,5] in biochemical and organometallic research. It provides a fascinating route to stereoregulated construction of heterocyclic frame[6]. Organomercurials are more advantageous than organolithium and Grignard reagents in the syntheses of metal-carbon σ-bonded compounds due to their less sensitivity towards air and moisture[7]. The sites of mercuration of aromatics are electron population controlled and the stability of the products arise from the conformation of the substrate[4,5]. In our earlier report[4] we have suggested the regioselectivity of mercuration of thioazomethines. Herein we give an account of the mercuration of 2-(benzylthio)-N-(benzylidene)anilines and the regioselectivity established by spectroscopic studies.



(i) EtOH/Na, $PhCH_2Cl$; (ii) ArCHO/EtOH; (iii) $Hg(OAc)_2$/dry MeOH; (iv) $LiCl.H_2O$.

Scheme I

Results and Discussion

The synthesis of Schiff bases **2** and their mercuration are shown in Scheme I. The ligands were synthesized following the reported procedure[8] by the condensation of 2-benzylthio-aniline **1** with *para*-substituted benzaldehydes in ethanol. The mercuric chloride derivatives **4** of the corresponding azomethines were prepared by *in situ* reaction of the ligands with $Hg(OAc)_2$ (1:1 molar ratio) in refluxing dry MeOH for 2 hr followed by the addition of LiCl.

The IR spectra of **4** indicate that all the mercurated derivatives are composed of one of Schiff base unit [ν(C=N), 1625-1640 cm^{-1}] and one Hg−Cl group [ν(Hg-Cl), 325-335 cm^{-1}]. The ν(C=N) remains almost unshifted on mercuration and gives an indication of free azomethine group. The ν(C−S) mode of the ligands **2** at 755-760 cm^{-1} remains almost unshifted in complexes **3** and **4** and the absence of ν(Hg−S) suggests noncoordination of thioether group[9]. The acetato complexes **3** exhibit strong bands at 1540-1555 [ν_{as}(COO)] and 1315-1325 cm^{-1} [ν_s(COO)] ($\Delta\nu$ = 225-230 cm^{-1}) corresponding to unidentate character of the bonded −COO group[10].

The complexes are almost insoluble in common organic solvents like benzene, acetonitrile, chloroform. The UV-Vis spectra of the ligands and com-

plexes, recorded in DMSO, are comparable; ligands **2** show two bands, 360-400 nm and 280-290 nm which are assignable to intraligand charge transfer bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively[8], and in complexes these bands are blue shifted by 15-25 nm.

The position of mercury atom was determined by ^1H NMR measurements. The NMR spectra are somewhat complex due to overlapping of benzyl protons in aromatic region and almost insensitive to the substitution in other aromatic nuclei. The protons in the two benzene nuclei about C=N group are assigned as C-phenyl (A ring) and N-phenyl (B ring) protons with their atom numbering as shown in Scheme I. These protons have been completely assigned on the basis of spin-spin structure and changes occurring therein on substitution. The N-phenyl or B-ring protons appear at higher field in comparison to C-phenyl protons[4,8]. The C-phenyl protons are highly sensitive to the substituent R in the aromatic aldehyde moiety. The shift of signals is in accord with the inductive and resonance effect of the group R. For methyl substitution (**2b** and **4b**) the signals suffer a shift to higher field due to electron releasing effect via inductive effect. The maximum upfield shifting as expected is observed in methoxy derivatives (**2c** and **4c**) for 10- and 12-H. The reverse effect is seen in **2c** and **4c**. The electron withdrawing character of $-NO_2$ shifts the signals considerable downfield. The mercuration has little effect on the chemical shift values of these protons. The higher field signals are due to protons of B- and C-ring. These signals suffer a little perturbation on substitution in **2**. The C-ring protons appear as overlapped multiplets (5H) in the region 7.25-7.40 ppm and difficult to assign. The signals of four B-ring protons (4H) appear at different field positions and suffer considerable change on mercuration in **4**. The most significant feature is the loss of resonance due to 4-H of B-ring from the spectra and the appearance of a new singlet. There are two *AB* type doublets (2H) and a singlet (1H) which suffer significant downfield shift compared to the peaks in the free ligands **2** and do not vary with different substituents (R). Assignments are shown schematically in Figure 1. The ^1H NMR data are compiled in Table I. This clearly shows that mercury atom is directed to the *para*-position of the N-phenyl ring rather than *ortho*-position of the C-phenyl which is the usual position for cyclometallation of the Schiff bases[8]. Sulfur coordination is also excluded as the $S-CH_2$ signal remains unaffected[4,11].The azomethine proton signal also remains almost unaffected by electrophilic substitution and supports mercuration of the N-phenyl ring.

The electron density distribution and conformation of the substrate determine the electrophilic substitution by $Hg(OAc)^+$ at *ortho*- and *para*-positions in the unsubstituted N-phenyl Schiff base[5,12] and account for the regioselectivity of the

Table I—^1H NMR spectral data[a] of compounds **2** and **4** (chemical shifts in δ, ppm and *J* values in Hz given in parentheses)

Compd	3-H	4-H[c]	5-H	6-H[b]	7-H[d]	9, 13-H[b]	10, 12-H	11-H	14-H[d]	16- to 20-H[e]
2a	6.95[b] (9.0)	7.08 (8.5)	7.08[c] (8.5)	7.16 (9.0)	8.47	7.98 (8.5)	7.65[c] (8.5)	7.65[c] (8.5)	4.31	7.28-7.34
2b[f]	6.96[b] (9.0)	7.10 (8.5)	7.10[c] (8.5)	7.15 (9.0)	8.32	7.81 (9.0)	7.34[b] (8.5)		4.22	7.25-7.30
2c[g]	6.92[b] (9.0)	7.08 (8.5)	7.08[c] (8.5)	7.16 (9.0)	8.39	8.02 (9.0)	7.19[b] (9.0)		4.27	7.24-7.28
2d	6.99[b] (9.0)	7.15 (8.5)	7.15[c] (8.5)	7.20 (9.0)	8.49	8.09 (9.0)	7.69[b] (9.0)		4.33	7.30-7.36
2e	7.03[b] (9.0)	7.20 (8.5)	7.20[c] (8.5)	7.24 (9.0)	8.59	8.16 (9.0)	8.38[b] (9.0)		4.38	7.34-7.40
4a	7.56[d]		7.33[b] (9.0)	7.26 (9.0)	8.53	8.02 (9.0)	7.68[c] (9.0)	7.68[c] (9.0)	4.35	7.30-7.35
4b[f]	7.57[d]		7.30[b] (9.0)	7.24 (9.0)	8.45	7.80 (8.5)	7.40[b] (8.5)		4.24	7.25-7.32
4c[g]	7.54[d]		7.28[b] (9.0)	7.23 (9.0)	8.47	8.06 (8.5)	7.21[b] (8.5)		4.29	7.24-7.30
4d	7.56[d]		7.36[b] (8.5)	7.25 (8.5)	8.55	8.14 (9.0)	7.73[b] (8.5)		4.35	7.32-7.40
4e	7.63[d]		7.40 (9.0)	7.30 (9.0)	8.67	8.29 (8.5)	8.42[b] (8.5)		4.42	7.35-7.40

[a], solvent $CDCl_3$ for **2** and DMSO-d_6 for **4**; [b], doublet; [c], triplet; [d], singlet, [e], multiplets [f], Me: (**2b**) 2.41; (**4b**), 2.43 ppm; [g], OMe : (**2c**), 3.82; (**4c**), 3.85 ppm.

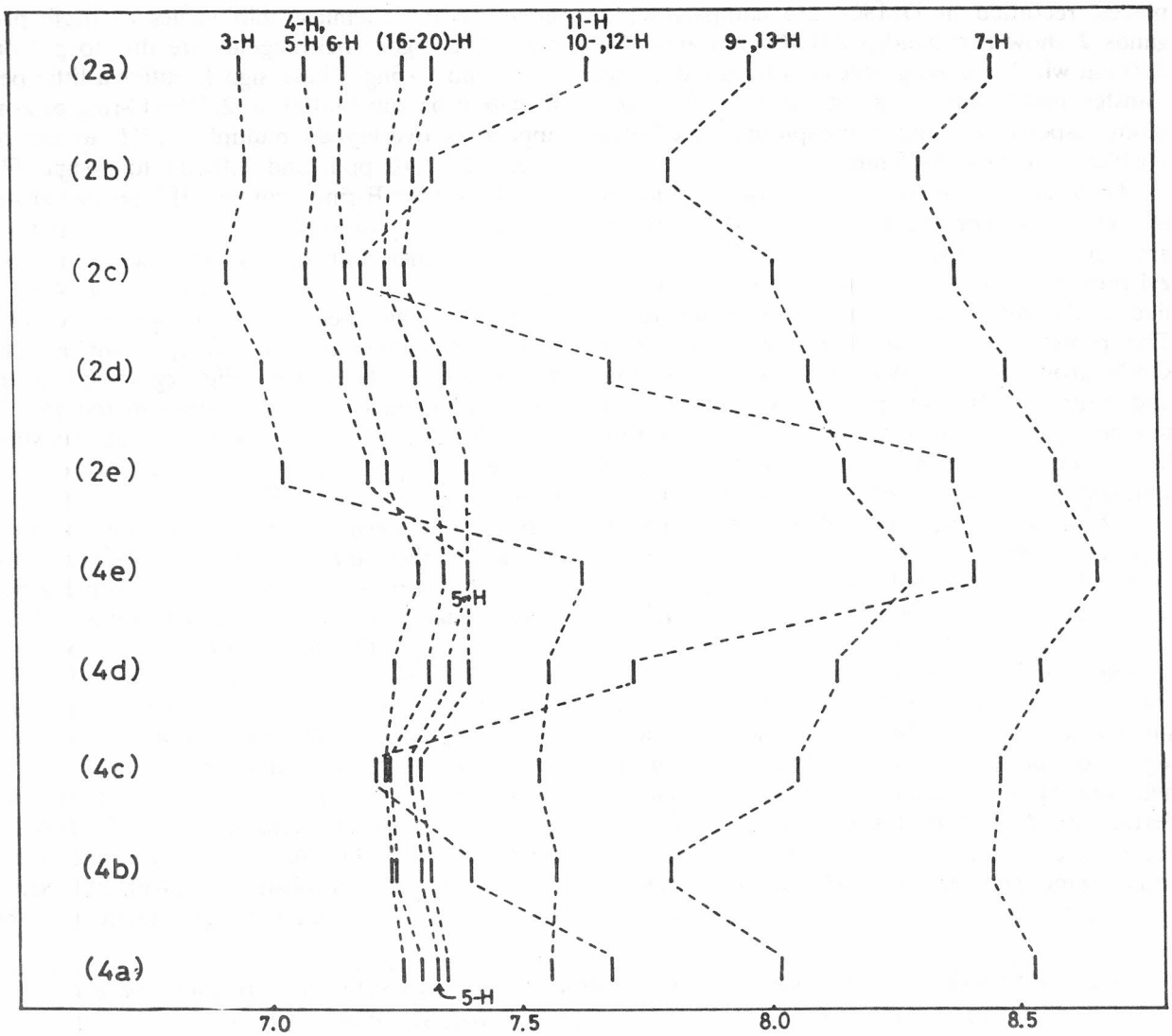


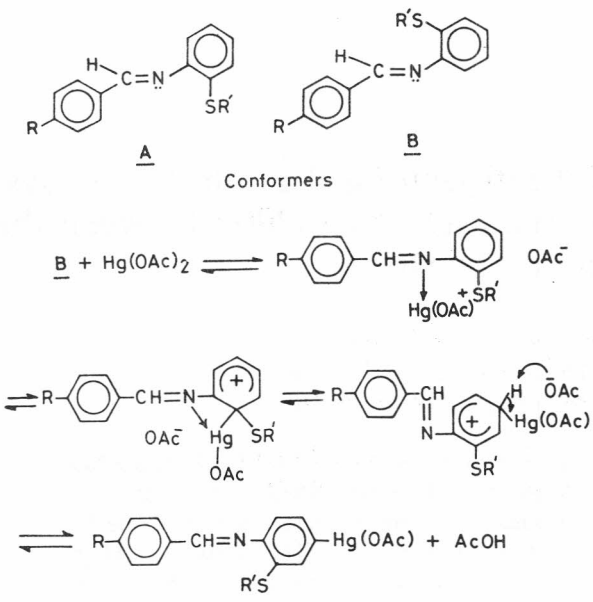
Figure 1—Schematic ^{1}H NMR spectra of the ligands **2** and chloromercury derivatives **4**.

process. The stability of a particular conformation is associated with the interactions of electron clouds in C−H or C−C bonds and various other electron rich bonds or groups[4,8]. In this particular case the stable conformation is **A** because of larger orbitals, lower electronegativity of sulfur and greater polarisation of S−C bond in S−CH_2Ph, and the other conformation **B** will be destabilized by stronger electronic interaction with azomethine C−H bond[4].

The established mechanism[13] of mercuration of N-substituted aromatics is the N-coordination to $Hg(OAc)^+$ followed by π-complex formation, and results in the electrophilic substitution on N-phenyl ring. Herein the coordination of azomethine-N to $Hg(OAc)^+$ accelerates the π-complex formation with N-phenyl ring as it is of higher electron density ring[12] which is reflected by higher field shifting of N-phenyl protons in ^{1}H NMR spectra. But 2-benzylthio group in the stable conformer **A** may block the substitution at the nearest position and direct the electrophile to *para*-position in the N-phenyl ring as shown in Scheme II.

Experimental Section

General. Solvents used in the reactions were of reagent grade and were dried by reported procedures[4]. $Hg(OAc)_2$ was purchased from Loba Chemie. Benzaldehyde, *p*-tolualdehyde and *p*-anisaldehyde were obtained from S.D's Fine Chem. Ltd. *p*-Chlorobenzaldehyde, *p*-nitrobenzaldehyde, benzyl bromide and 2-aminothiophenol were of reagent grade from E Merck.



Scheme II – Plausible mechanism of mercuration

Metallic sodium was obtained from Lokenath Research Laboratories.

The elemental analyses were carried out on a Perkin-Elmer 240C elemental analyser. IR spectra were recorded on a Perkin-Elmer 783 or 883 spectrometer, ^{1}H NMR spectra on a Varian Gemini 300 MHz NMR spectrometer in $CDCl_3$ for **2** and DMSO-d_6 for **4**, and UV-Vis spectra on a Shimazdu 160A spectrometer. Conductivity was tested on a Sytronics 304 model digital conductivitimeter.

The ligands **2** were synthesized by a two-step synthetic route. 2-Benzylthio-aniline **1** was prepared by the literature procedure[8]. The required Schiff bases **2** were obtained by condensing **1** with aldehydes in equimolar proportions. The details of a representative case are given below.

To an ethanolic solution (10 mL) of 2-benzylthio-aniline **1** (1 g, 4.66 mmoles) was added dropwise an alcoholic solution (10 mL) of benzaldehyde (0.5 g, 4.7 mmoles) and the reaction mixture stirred 2 hr. An orange crystalline product separated out slowly. It was filtered, washed with cold EtOH, dried over $CaCl_2$, and recrystallised from mixture of chloroform and ethanol, yield 65%. For other ligands the yield was 60-75%. Their melting point are **1a**, 92 ± 2°; **1b**, 104 ± 1°; **1c**, 102 ± 1°; **1d**, 62 ± 2°; **1e**, 152 ± 2°.

All the complexes were synthesized according to a common procedure as given for **4a**: A solutionof $Hg(OAc)_2$ (0.30 g, 0.94 mmole) in dry MeOH (10 mL) was added dropwise to a solution of 2-benzylthio-N-benzylideneaniline **2a** (0.3 g, 0.99 mmole) in the same solvent (10 mL). The mixture was stirred and refluxed for 1 hr. At the end of the reaction, the mixture was allowed to cool down to room temperature, LiCl. H_2O (0.13 g, 2.15 mmoles) in MeOH added and the resulting thick mixture stirred for 20 min. The light yellow precipitate was filterd, washed with ether, dried *in vacuo*, and crystallised from DMSO-MeOH mixture, yield, 75%. The yield of other complexes was 70-90%. Satisfactory elemental analyses were obtained for all the members of series **2** and **4**.

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