

## NOTES

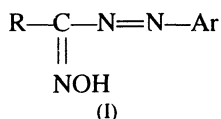
## Synthesis and Studies of Some New Arylazooximes and their Cobalt(III) Chelates

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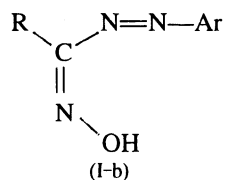
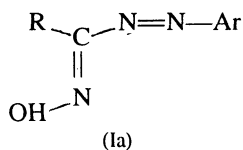
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In the present communication, we synthesised new arylazooximes, (R = *o*-, *m*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, *o*-, *p*-ClC<sub>6</sub>H<sub>4</sub>, *p*-Br(C<sub>6</sub>H<sub>4</sub>) *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; Ar = C<sub>6</sub>H<sub>5</sub>) to study whether the nature of R has any effect on the structure and geometry of the azooxime and their Co(III) complexes.

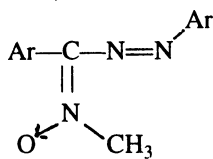


During the present investigation on these azooximes we found that these azooximes behave in a similar manner, irrespective of the type of substitution on R.  $\nu_{\text{NO}}$  of all the oximes appears between 1050–950 cm<sup>-1</sup>. In most of the cases this absorption, typical of the oximes in general<sup>1</sup>, appears as a doublet of a very high intensity.  $\nu_{\text{OH}}$  appears as a strong and broad absorption around 3600–2800 cm<sup>-1</sup> indicating the strong intermolecular hydrogen bonding in the solid phase. There is no strong band around 1600–1500 cm<sup>-1</sup> and 1400–1150 cm<sup>-1</sup> characteristic of monomeric and dimeric nitroso compounds respectively<sup>2</sup>. Moreover, these azooximes show electronic absorption at 400–420 nm and 300–330 nm characteristic of azo compounds.<sup>3</sup> No electronic absorption of the nitroso group between 600–800 nm could be located for these azooximes.<sup>4</sup> The above data clearly exclude the nitroso structure, II, and establishes the oxime structure, I, for these compounds irrespective of the nature of R.

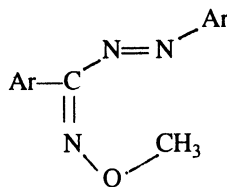
The proton magnetic resonance spectrum of one of these compounds namely, I (R = *p*-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; Ar = C<sub>6</sub>H<sub>5</sub>) shows two —OCH<sub>3</sub> signals at 3.96 to 4.00 ppm from TMS in CDCl<sub>3</sub> indicating the presence of two geometric isomeric forms Ia and Ib in solution. Although PMR alone is not very helpful in determining the geometry of other oximes prepared (because of the complexity of the resonance signals of aromatic protons), it may be inferred that these azooximes exist in both the isomeric forms (Ia) and (Ib) in CDCl<sub>3</sub> because—



- (i) The spread and the number of lines of their aromatic protons signal decrease on methylation (the methylation is known to produce only the less sterically hindered isomeric species (IIa and IIb) in each of these cases).<sup>5</sup>



(II-a)



(II-b)

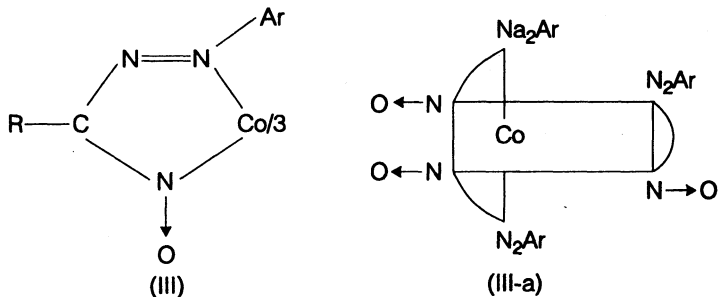
- (ii)  $\nu_{\text{NO}}$  of these compounds generally appears as a doublet of very strong intensity.
- (iii) The bulk of (R = aryl) of the newly synthesised azooximes and those of the already studied I (R =  $\text{C}_6\text{H}_5$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$  etc.) is same and the latter are already known to exist in both the isomeric forms (Ia) and (Ib).<sup>6</sup>
- (iv) The OH proton signals of all the newly prepared azooximes of aromatic aldehydes in a H-bonding solvent like pyridine appears as a closely spaced and broad doublet strongly indicating the presence of both the isomers (Ia) and (Ib).

TABLE I  
IMPORTANT IR FREQUENCIES ( $\text{cm}^{-1}$ ) OF SOME ARYLAZOOXIMES AND THEIR  
TRIS(ARYLAZOOXIMATO)Co(III) COMPLEXES

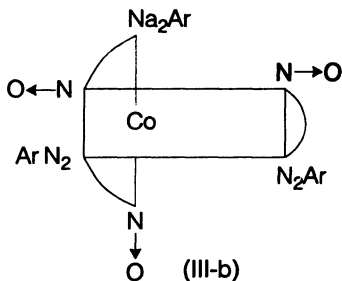
Compound	$\nu(\text{NO})$	$\nu(\text{C}=\text{N})$
I (R = $o\text{-ClC}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	980, 1050 doublet (vs)	1650
I (R = $p\text{-OCH}_3\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1000 broad (vs)	1650
I (R = $m\text{-NO}_2\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1950 broad (vs)	1630
I (R = $o\text{-NO}_2\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1030, 1970 doublet (vs)	1635
I (R = $p\text{-BrC}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	995, 1040 doublet	1645
IV (R = $p\text{-OCH}_3\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1340 (s)	1610 (ms) $\nu(\text{C}-\text{O})$ (1250, 1170) (s)
IV (R = $o\text{-ClC}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1250 doublet (vs)	1640 (ms) $\nu(\text{NO}_2)$ (1530, 1340) (vs)
IV (R = $o\text{-NO}_2\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1260 doublet (vs)	1620 (ms)
IV (R = $m\text{-NO}_2\text{C}_6\text{H}_4$ ; Ar = $\text{C}_6\text{H}_5$ )	1235 (s)	1620 (w) $\nu(\text{NO}_2)$ (1530, 1340) (vs)

The newly synthesised azooximes immediately react with Co(II) or Co(III) compounds to give tris(arylazooximate) Co(III). The yield of these chelates is nearly quantitative as shown by TLC and column chromatography on alumina. Only a single isomeric species which is easily eluted with benzene and hexane mixture could be isolated in all these cases indicating the formation of only one geometrical isomer of these complexes. The IR data shows these chelates to have a nitronic structure (IV) (the  $\nu(\text{N}-\text{O})$  appears between  $1300\text{--}1200\text{ cm}^{-1}$ ,  $\nu(\text{N}-\text{N})$  appears as a weak absorption band around  $1400\text{ cm}^{-1}$ ,  $\nu(\text{C}-\text{N})$  appears between  $1630\text{--}1600\text{ cm}^{-1}$  (Table I). The strong absorption around  $1000\text{--}950\text{ cm}^{-1}$  in azooximes completely disappears in the IR of these tris chelates of Co(III). The pmr of one of the III (R =  $p\text{-OCH}_3\text{C}_6\text{H}_4$ ; Ar =  $\text{C}_6\text{H}_5$ ) shows three closely spaced

$-\text{CH}_3$  signals at 3.88, 3.86, 3.83 ppm from TMS in  $\text{CDCl}_3$  indicating a *trans* geometry (IIa,  $\text{R} = p\text{-OCH}_3\text{C}_6\text{H}_4$ ). The formation of only *trans* isomer (III-a) of III may be due to the steric coupled with statistical considerations. (The *cis* isomer, IIIb, on the basis of statistical considerations alone should be found in lesser quantities. Apart from this, all the three bulkier Ar groups in the *cis* isomer (IIIb)



are overcrowded on one triangular face of the octahedron making it less stable). It may thus be inferred that the tris chelates (III) which exist in only one isomeric form, have only *trans* geometry (IIIa) rather than IIIb. The PMR data on other newly synthesised (II) is not very conclusive, but since only a single isomer is isolable in all these cases, it may be inferred<sup>7,8</sup> that these tris chelates of Co(III) may also exist in the less sterically hindered *trans* form (IIa).



Similar conclusion was drawn in an earlier study on the Co(III) chelates of some already known azooximes.<sup>9</sup>

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