Heterocyclic ring formation via intramolecular coordination of hydroxyl oxygen of carboxyl group to arsenic(V) in o-carboxyphenylmethyldialkyl/arylarsonium iodides

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IR, PMR and mass spectral data of o-carboxyphenylmethyldialkyl/arylarsonium iodides [(2a): R = Me, Ph or p-tolyl] favour the formation of a five-membered heterocyclic ring (2c) through intramolecular coordination of hydroxyl oxygen of carboxyl group to arsenic(V). This is in contrast to the reported heterocyclic ring formation via intramolecular coordination of carbonyl oxygen to arsenic(III) in o-carboxyphenylarsonous dichloride (Ia).

The stretching mode of the carbonyl group in aromatic carboxylic acid dimers is normally observed at 1680-1700 cm⁻¹ and shifts to higher frequency when the phenyl ring is substituted by an electron attracting group. The appearance of ν CO band at 1660-1680 cm⁻¹ in the spectra of o-carboxyphenylmethyldialkyl/arylarsonium iodides [(2a): R = Me, Et, C₆H₄OH, Ph or p-tolyl] has been explained in terms of arsenic lone pair coordination with the o-phenylene ring which is maximum for R = Me or Et²³. Here the CO₂H group does not coordinate to arsenic(III). On the other hand, the appearance of this band at 1653 cm⁻¹ in the spectrum of o-carboxyphenylarsonous dichloride [(1a): R = Cl] has been attributed to the intramolecular coordination of the carbonyl oxygen of the acid dimer to arsenic(III) as shown in structure (1b)⁴. The results of PMR and mass spectral studies on o-carboxyphenylmethyldialkyl/arylarsonium iodides [(2a): R = Me, Ph or p-tolyl], however, suggest that intramolecular coordination of the acid dimer to arsenic(V) takes place through hydroxyl oxygen. We present here the results of our studies on this system.

Experimental

Tertiary arsines [(1a): R = Me, Ph or p-tolyl] were prepared by using reported method⁴. These were converted into the corresponding methiodides (2a) by reacting 1 g of the sample dissolved in EtOH (10 cm³) with three-fourths excess of MeI under reflux and subsequent precipitation by the addition of excess of Et₂O; and were characterized on the basis of reported melting points. IR spectra (4000-200 cm⁻¹) were recorded in KBr pellets on a PYE UNICAM SP3-300 spectrophotometer. PMR spectra were recorded in CDCl₃ on a Jeol JNM-PMX 60SI NMR spectrometer using TMS as internal standard while the mass spectra were recorded on Jeol-JMS-OISG-2 instrument at RSIC, CDRI, Lucknow.

Results and discussion

The methiodides [(2a): R = Me, Ph and p-tolyl] were prepared for the first time⁵ by our group in 1970. The appearance of ν CO band at ~ 1700 cm⁻¹ in comparison to the bands at 1660-1680 cm⁻¹ in the spectra of the parent arsines (1a) was explained in terms of the electron withdrawing nature of the arsionium ion⁶. The absence of the M⁺ (molecular ion) peaks at m/z 492 for R = Ph and at 520 for R = p-tolyl and the presence of peaks corresponding to (M⁺-H) ion also rule out structure (2b) in favour of (2a). The observed peak due to (M⁺-I-H) ion at m/z 364 for R = Ph and at 392 for R = p-tolyl corresponds to the formation of the cyclic ion 1-methyl-1,1-diaryl-2,1,3-benzoxarsol-3-one (3).
However, the observed singlets at \( \delta 1.30 \text{ ppm (6H)} \) [cf. \( \delta 1.25 \text{ ppm (6H)} \) in (1a); \( R = \text{Me} \); ref. 3] due to two methyl groups and \( \delta 3.00 \text{ ppm (3H)} \) due to the third methyl group in the PMR\((\text{CDCl}_3)\) spectrum of (2a): \( R = \text{Me} \) clearly point out the total inhibition of the free rotation of the methyl groups around As-C aromatic bond. This lack of rotation and raising of the \( v \text{ CO} \) value of \( 1660 \text{ cm}^{-1} \) in (1a) \( R = \text{Me} \) to \( \sim 1700 \text{ cm}^{-1} \) can be explained only in terms of heterocyclic structure (2c) formed through the intramolecular coordination of the hydroxyl oxygen of the carboxyl group to arsenic(V). The structure (2c) also holds good for its phenyl and p-tolyl analogues in view of similar \( v \text{ CO} \) value of \( \sim 1700 \text{ cm}^{-1} \) and PMR signal (singlet) at \( \delta 3.00(3H) \) due to methyl protons.

The reported intramolecular coordination of the carbonyl oxygen to arsenic(III) in some benzophenones [(4): \( R = R' = \text{Cl}; R = \text{Ph}; R' = \text{Cl} \) and (5)] has been considered to be stabilized by arsenic lone pair conjugation with the aromatic ring\(^7\). The inability of the carbonyl oxygen to coordinate to arsenic(V) in (6), as shown by X-ray analysis\(^8\), is consistent with the absence of the lone pair on arsenic(V). If lone pair conjugation were the only factor stabilizing the intramolecular coordination, the hydroxyl oxygen of the CO\(_2\)H would have not coordinated to arsenic(V) to yield (2c). Thus, it is the smaller size of arsenic(V) compared to that of arsenic(III) that keeps it away only from the carbonyl oxygen and not from the hydroxyl oxygen which is singly bonded to carbon and coordinates to arsenic(V).

It can be concluded that the coordination of carbonyl oxygen to arsenic(III) in (1b) is stabilized by arsenic size factor as well as lone pair conjugation while the coordination of hydroxyl oxygen to arsenic(V) in (2c) is stabilized by the size factor alone.

The importance of the size factor is also supported by a single crystal X-ray report on \( o \)-carboxyphenyl-diphenylarsine oxide (7a)\(^9\) which shows it to exist as a novel structure (7b) where it is the carboxylate oxygen (C \( \equiv \) O) that is bonded to arsenic(V). The third factor which explains the presence of intramolecular coordination in (1a) for \( R = \text{Cl} \) (1b) and not for \( R = \text{Me, Et, C}_6\text{H}_{11}, \text{Ph} \) or p-tolyl has been reported\(^2\) to be the inductive effect of the group attached to arsenic, i.e., the electron withdrawing chlorine makes arsenic(III) an acceptor while an alkyl or aryl group makes it a good donor as evidenced by the formation of the adduct Me\(_3\)As\(\rightarrow\)AsCl\(_2\)Et\(^{10,11}\).

References