

A Structural Reinvestigation of the Reported Anhydride† from *o*-HO₂As(C₆H₄CO₂H)₂: Novel Spirobicyclic & Tricyclic Acyloxy(carboxy)arsorane Structures

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A detailed examination of the IR, TG, DTG, DTA and acid equivalent data shows that the attempt to prepare *o*-HO₂As(C₆H₄CO₂H)₂ (3a) did not yield its anhydride (4a) as claimed [J chem Soc, 1924, 2025] but its impure isomer, monohydrate of (4a), which has been characterised now as the first novel tricyclic acyloxy(carboxy)arsorane (3b) in solid phase. The compound (4a) has now been prepared for the first time by the dehydration of (3b) and is shown to exist as intermolecularly H-bonded spirobicyclic acyloxy(carboxy)arsorane (4b).

In our earlier communications^{1,2} we have shown that *o*-carboxyphenylarsonous acid (1a)^{3,4} and *o*-carboxyphenylarsonic acid (2a)^{3,5} actually exist as benzoxarsole monohydrates (1b) and (2b) respectively. We now report the results of a reinvestigation into the characterization of the anhydride (4a) reported to be isolated during an unsuccessful attempt to prepare *o*-HO₂As(C₆H₄CO₂H)₂ (3a)³.

Materials and Methods

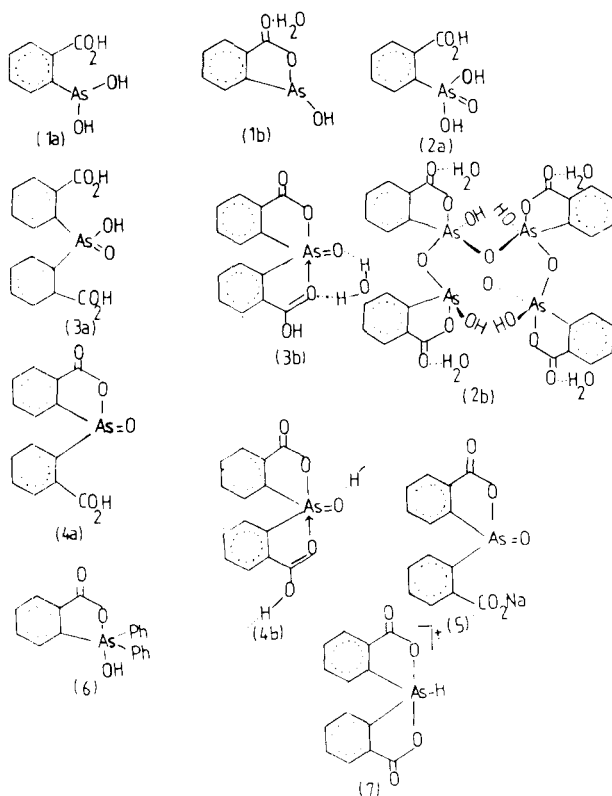
Commercially available chemicals were used without purification. The benzoxarsole monohydrate (1b) earlier known as *o*-carboxyphenylarsonous acid or *o*-benzoarsenious oxide was prepared by the literature method³.

Infrared spectra (4000-200 cm⁻¹) were recorded in KBr pellets/CH₂Cl₂ on a PYE-UNICAM SP3-300 spectrophotometer. ¹H NMR spectra were recorded on a Jeol JNM-PMX 60SI NMR spectrometer using TMS as internal standard. Mass spectra were recorded on Jeol-JMS-01SG-2 instrument at CDRI, Lucknow. The thermal analysis of (3a) and (4a) were carried out on an STA 780 thermobalance.

Preparation of 1-oxy-1-(*o*-carboxyphenyl)-3H-2,1-benzoxarsol-3-one monohydrate (3b)

The reported outline³ for the preparation of (4a) has been developed into the following procedure.

A solution of anthranillic acid (9g) in a mixture of hydrochloric acid (13 cm³) and water (72 cm³) was diazotized with a saturated solution of NaNO₂ (5g) at -5°C. Sodium *o*-benzarsenite solution was prepared by dissolving (1b) in a freshly prepared hot solution of NaOH (2g) in distilled water (34 cm³) and to it a saturated solution of CuSO₄·5H₂O (0.2 g) was added. The diazotized solution was added to this *o*-benzarsenite solution in small portions at 0°C with constant stirring which was continued for 10 min after the complete addition. Reaction mixture was heated at 60°C for 2h, cooled and acidified with dilute hydrochloric acid. The resulting brown solid was filtered and crystallized first from MeOH and then from boiling water. A pure white compound obtained after a few crystallizations from water, melted at 254-5°C (the reported³ m.p.). Acid equivalent 308 (found) and 305, 312 (re-

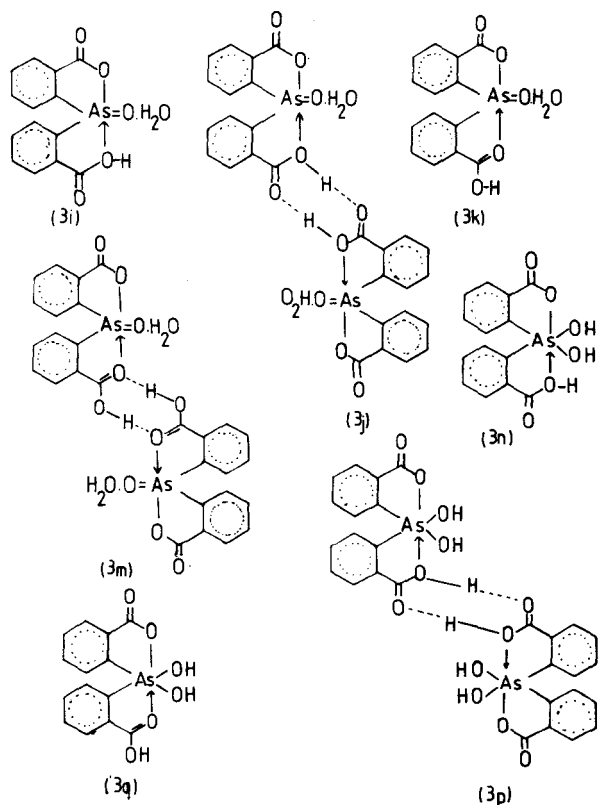


† 1-Oxy-1-(*o*-carboxyphenyl)-3H-2,1-benzoxarsol-3-one.

ported³). Further repeated crystallizations from water could improve the m.p. upto 282-3°C. Acid equivalent 346.7 (found) and 350.0 (reqd.); I.R. (cm^{-1}) (KBr) 3535w, 3420w, 3080w, 3020vw, 2350vw, 1705ssh, 1685s, 1580w, 1460m, 1335s, 1280s, 1250s, 1170w, 1125m, 1050w, 970w, 842m, 810vw, 780w, 752s, 725vw, 680m, 570vw, 480m, 400m, 320s, 300w; ^1H NMR (DMSO) δ 7.8 (8H, m, ArH); mass: m/z 350(M^+ , n.o.), 316($\text{M}^+ - \text{H}_2\text{O} - \text{O}$), 288($316 - \text{CO}$), 244($288 - \text{CO}_2$), 243($244 - \text{H}$), 228($244 - \text{O}$), 227($228 - \text{H}$), 196($316 - \text{C}_6\text{H}_4 - \text{CO}_2$), 195($196 - \text{H}$), 181($\text{C}_6\text{H}_5\text{COC}_6\text{H}_4^+$), 152($196 - \text{CO}_2$), 151($195 - \text{CO}_2$), 139($195 - \text{C}_2\text{O}_2$), 105($196 - \text{AsO}$), 91(AsO^+).

Preparation of 1-oxy-1-*o*-carboxyphenyl)-3H-2,1-benzoxarsole-3-one (4a)/(4b):

A solution of [(3b), (0.2g)] in TFA (10 cm^3) was refluxed for 4h and the excess solvent was removed by vacuum distillation. A gum was obtained which solidified after keeping *in vacuo* for 2hr. The crude compound thus obtained was recrystallized from dry benzene m.p. 282-3°C. The dehydration of (3b) to (4a)/(4b) can also be achieved by refluxing in benzene, treatment with anhydrous AlCl_3 in CH_2Cl_2 or heating at 110°C. Acid equivalent: 330.5 (found), 332.0 (reqd.); ^1H NMR (DMSO): δ 7.83 ppm (8H, m, ArH); IR (cm^{-1}) (KBr): 3115vw, 3080vw, 2370vw, 1740s, 1685s, 1580w, 1450m, 1320m, 1285m, 1285w, 1270m, 1230m, 1160sh, 1130w, 1108w, 1040m, 1018w, 970vw, 842s, 800w, 770w, 745m, 715w,



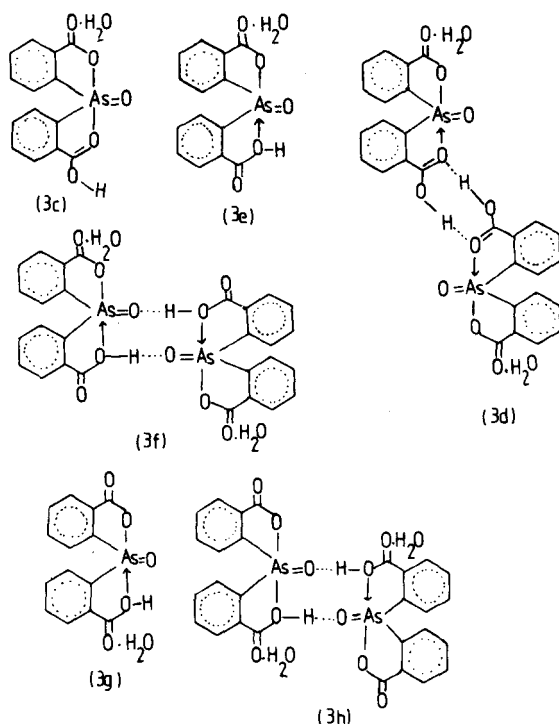
675s, 470s, 392s, 320w, 270vw; the mass spectrum is identical with that of (3b).

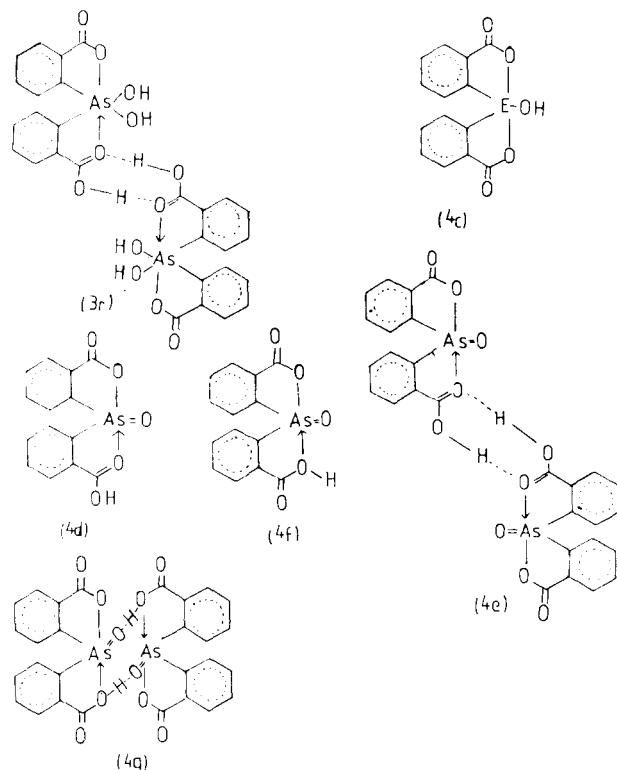
Preparation of Monosodium salt (5)

A solution of the compound [(3b), (0.2 g)] in MeOH (10 cm^3) was titrated against a saturated NaOH solution using phenolphthalein as indicator. The solid salt formed in solution was separated azeotropically m.p. 300°C; IR cm^{-1} (KBr) 3500b, 3085w, 2400vw, 2360vw, 1975vw, 1670bs, 1590s, 1460m, 1420m, 1340m, 1290m, 1260m, 1150m, 1130m, 1055m, 890s, 845m, 812w, 752s, 720w, 690m, 575vw, 480m, 395m, 258w.

Results and Discussion

The improvement in the melting point from 255 to 282-3°C and in the acid equivalent value from 308 to 346.7 on further recrystallizations from water proves that the compound (m.p. 255, acid equivalent 308) considered by Aeschlimann and McClelland³ to be the anhydride (4a) is actually the contaminated form of its monohydrate [m.p. 282-3°C, acid equivalent 346.7 (Reqd 350)]. The anhydride (4a) has now been obtained for the first time by the treatment of the monohydrate with TFA/ AlCl_3 , refluxing in C_6H_6 or heating it at 110°C and has the expected acid equivalent value (Found 330.5, Reqd 332). The presence of water in the monohydrate is also confirmed by its TG curve which shows the loss of one water molecule





(Found 5%, Req'd 5.14%) between 80 and 107°C. This change is associated with the appearance of DTG and endothermic DTA peaks at 94°C. The anhydrous intermediate is stable upto 204°C and then loses half water molecule upto 284°C (DTG and endothermic DTA peaks at 258°C). The thermal analytical data of the anhydride (4a) show, as expected, the loss of only half water molecule at 204-284°C.

The appearance of two bands at 1705-45 and 1685 cm^{-1} in the $\nu\text{C}=\text{O}$ region in the solid state IR spectra of (4a) and its monohydrate suggests the presence of two types^a of carbonyl groups but the absence of $\nu\text{As}=\text{O}$ (800-900 cm^{-1})^b, δOH (900-950 cm^{-1}) and νOH (2500-2700 cm^{-1}) bands² indicates the absence of the $\text{As}=\text{O}^c$ and dimeric CO_2H^d groups. The high energy $\text{C}=\text{O}$ band is missing in the spectrum of their monosodium salt (5) which contains only one $\nu\text{C}=\text{O}$ band at 1675 cm^{-1} . Thus, the band present at 1675-85 cm^{-1} in all the three spectra may be attributed to $\nu\text{C}=\text{O}$ of benzoxarsole ring⁶. The second $\nu\text{C}=\text{O}$ band present only in the spectra of the

^aRules out (3a) and (4c), ^b $\nu_{\text{As}=\text{O}}$ band at 890 cm^{-1} in (5); two bands at 800 and 845 cm^{-1} appear in each of the spectra of (3b), (4b) and (5). ^cRules out (3c), (3d), (3g), (4a), (4d) and (4f). ^dRules out (3d), (3j), (3m), (3p), (3r) and (4e).

^eRules out (4f) and (4g) for which $\nu_{\text{C}=\text{O}}$ is expected at 1785 cm^{-1} . ^fRules out (3g), (3h), (3k) and (3i) since for the first three the band is expected at $\sim 1740 \text{ cm}^{-1}$ and for the last one at 1785 cm^{-1} .

^gFavours (3a), (3n), (3p), (3q) and (3r) but all of these fail to explain the observed acid equivalent value.

first two compounds may be ascribed to the monomeric CO_2H group. This assignment is supported by the appearance of ν_{OH} band at 3100 and 3545 cm^{-1} in the spectra of (4a) and its monohydrate respectively. The lowering of $\nu_{\text{C}=\text{O}}$ value from 1785 cm^{-1} (in PhCO_2H monomer)⁷ to 1745 cm^{-1} in the spectrum of (4a) may be explained in terms of its solid state structure (4b) which contains intramolecular coordination of the carbonyl oxygen to arsenic(V). The further lowering of this $\nu_{\text{C}=\text{O}}$ value to 1705 cm^{-1} in the spectrum of the monohydrate may be attributed to the simultaneous H-bonding of the carbonyl oxygen with the water molecule which is also H-bonded to the $\text{As}=\text{O}$ oxygen in (3b). The absence of $\nu_{\text{As}=\text{O}}$ band and the presence of $\nu_{\text{OH}}(\text{As}-\text{OH})^g$ band^{8,9} at 2370 and 2350 cm^{-1} in the spectra of (4a) and its monohydrate respectively as well as the appearance of $\nu_{\text{OH}}(\text{H}_2\text{O})$ band at 3420 cm^{-1} in the latter spectrum and its absence in the former are also consistent with the proposed solid phase structures (4b) and (3b).

As expected for structures (3b) and (4b), their PMR(DMSO) spectra are almost identical but all the aromatic protons appear as a single multiple at $\delta 7.80$ and 7.83 ppm respectively (cf ^1H NMR spectrum of (6)⁹). The molecular ion peak is not observed in the mass spectra of (3b) and (4b) which are identical and contain the highest m/z peak at 316 that may be explained in terms of the formation of a stable spirobicyclic diacyloxy arsorane (7) ion corresponding to $(\text{M}^+ - \text{H}_2\text{O} - \text{O})$ and $(\text{M}^+ - \text{O})$ ions respectively.

It can, therefore, be concluded that the attempt to prepare (3a) by Aeschlimann and McClelland³ did not yield its anhydride (4a) as claimed but its impure isomer, monohydrate of (4a), which has been now purified and found to exist as the first novel tricyclic acyloxy (carboxy) arsorane structure (3b). The dehydration of the monohydrate (3b) yields the anhydride (4a) which exists as the first spirobicyclic acyloxy (carboxy) arsorane (4b). Thus, the anhydride (4a) and its monohydrate (3b) have been isolated for the first time during this reinvestigation.

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