

bond (5), while IIIb, IIIc and IIId show at about 400 cm^{-1} bands of the As-S bond (6).

Analogously to the antimony compounds (1) no equilibrium between tricoordinate and pentacoordinate forms like that observed for similar phosphorus compounds was observed (7). In fact, the ir spectra give no evidence of the As-H stretching bands at 2100 cm^{-1} (8), and the nmr spectra do not show any As-H signal at high or low fields.

We have determined the structure of the compounds IVa-c from elemental analytical data and by nmr, ir and mass spectra. The mass spectra give molecular ion peaks at m/e 474, 522 and 506, respectively; the nmr spectra show only aromatic signals, while the ir spectrum show characteristic bands of the $=\text{C}-\text{O}$, AsO-C, As-O and As-S bonds.

Spirane derivatives Va-c can be obtained by treating IIa-b with Ia or Ib in triethylamine. The compounds Va and Vc are also obtained by treating IIa-b with only hot triethylamine; in this case the yields are lower and traces of Ia or Ib are detected, the presence of which can be explained by partial cleavage of the As-O and As-Y bond of IIa-b. The presence of Ia or Ib can explain the pathway followed in the formation of the spirane compounds Va and Vc. In contrast with the literature data (2), these compounds are obtained as crystalline solids, that are crystallized from water. The coordination of the amine nitrogen with the arsenic, and not with the hydrogen of a possible OH, as other authors report (2), is supported by the absence of the OH characteristic stretching band and by the presence of the As-N band at $570\text{-}560\text{ cm}^{-1}$ (9). This structure is also confirmed from other ir data, nmr and mass spectra. Actually the mass spectrum shows the molecular ions corresponding to the deaminate molecule (at m/e 291, 307, 323, respectively) and the triethylamine (m/e 101). The nmr spectrum, besides the aromatic signals, shows a quartet at δ 3.00 ppm attributable to six methylenic hydrogens and a triplet at δ 1.30-1.10 ppm attributable to nine methylic hydrogens.

The compounds IIa-b easily react with sodium hydroxide, ethoxide and *p*-cresolate to give VIa-b, VIIa-b and VIIIa-b, respectively. All these compounds are converted to the oxides Xa-b at different rates; VIa-b gives water and Xa-b few hours after the preparation; VIIa-b within a month gave diethyl ether and Xa-b, while VIIIa-b was converted to Xa-b and *p*-tolyl ether only after many months. The same results are obtained when VIIa-b are prepared by reaction of Ia-b with triethoxyarsine.

In contrast with all these facts, the corresponding reactions with the analogous antimony compounds lead to 2-OR substituted compound only in one case (I). This compound is obtained at low temperature and quickly turns into the oxide, which is the only compound obtained at different temperatures. These reactions carried on according to the literature (10) always gave 2,2'-bi-(1,3,2-

benzodioxastibole)oxide; in these conditions it proved impossible to isolate the intermediate 2-ethoxy-1,3,2-benzodioxastibole.

The structure of the compounds VIa-b, VIIa-b, VIIIa-b and Xa-b has been unambiguously determined by elemental analysis and ir, nmr and mass spectra. The mass spectra show the characteristic molecular ions peaks; the ir spectra, besides the characteristic bands of $=\text{C}-\text{O}$, AsO-C, As-O bonds, show, in the case of the benzoxathiarsoles (VIb, VIIb, VIIIb, Xb), bands attributable to As-S bond and in the case of the compounds VIa-b bands of the OH group at $3440\text{-}3340\text{ cm}^{-1}$. The nmr spectra of the compounds VIa-b show either aromatic signals centered at δ 6.80 and δ 7.15 ppm respectively, either deuterium oxide exchanged signals at δ 8.85 and δ 6.30 ppm, respectively, attributable to the OH protons. The compounds VIIa-b show three signals centered at δ 6.90 and δ 6.95, δ 3.60 and δ 3.45, δ 1.10 and δ 1.00 ppm respectively, attributable to aromatic, methylenic and methylic protons. The compounds VIIIa-b show signals at δ 6.95 and δ 7.10, δ 2.30 and δ 2.20 ppm, attributable to aromatic and methylic protons respectively. The compounds Xa-b show only aromatic signals.

In contrast with the analogous VIIIa-b, the reaction of IIa-b with sodium *p*-toluenethiolate or *p*-toluenethiol gives the compounds IXa-b, that do not undergo any transformation even after many months.

When IIa-b are made to react with organolithium compounds, as *n*-butyllithium, they give 2-*n*-butyl derivatives XIa-b that confirm the possibility of preparing, by this way, 2-alkyl or 2-aryl substituted 1,3,2-benzodioxo- and 1,3,2-benzoxathiarsoles. Also this latter fact is in contrast with the analogous reactions of the antimony, that only give dimerization of the etherocyclic radical (1).

The structure of IXa-b and XIa-b have been demonstrated by elemental analysis and ir, nmr and mass spectra. The ir spectra of IXa-b, besides the frequencies of the already examined products, show characteristic bands of the As-S bonds, while XIa-b show bands attributable to As-C bond at 750 and $290\text{-}285\text{ cm}^{-1}$ (6, 11). The mass spectra show molecular ion peak. The nmr spectra of IXa-b show signals at δ 7.10 and δ 2.30 and δ 2.15 ppm, attributable to aromatic and methylic protons. The nmr spectra of XIa-b show signals centered at δ 6.90 and 7.00, δ 1.40 and δ 1.45 and δ 0.90 ppm, attributable to aromatic, methylene and methyl protons, respectively.

EXPERIMENTAL

Melting points were determined on a Tottoli apparatus (uncorrected). Ir spectra were recorded on a Perkin-Elmer model 325 spectrophotometer; compounds were examined in the range $4000\text{-}600\text{ cm}^{-1}$ using the pressed potassium bromide disk and in the range $700\text{-}200\text{ cm}^{-1}$ using Nujol mulls between cesium iodide plates. Nmr spectra were taken using a JEOL C-60 HL spectro-

meter; chemical shifts were measured in ppm (δ) using hexamethyldisiloxane as an internal standard. Mass spectra were determined on a "Hitachi" Perkin-Elmer RMU-6D spectrometer at 70 eV. Microanalyses for CHN were carried out on a Perkin-Elmer model 240 Elemental Analyzer; analyses for S and As were performed by the literature procedures (12).

2-Chloro-1,3,2-benzodioxarsole (IIa).

Method A.

A stirred solution of Ia (10 mmoles), arsenic trichloride (10 mmoles) and dry benzene (20 ml.) was refluxed until the hydrogen chloride vapours completely disappeared. The solvent was then removed in a rotary evaporator and the residue was sublimed *in vacuo*, yield 93%, m.p. 132° [lit. (13) m.p. 131-132°].

Method B.

To a stirred solution of Ia (10 mmoles) in dry benzene (10 ml.), kept at -5°, the dichloroethoxyarsine (14) (10 ml.) was added dropwise under nitrogen. When the addition was completed, the mixture was stirred for almost five hours. The precipitate, filtered off, was identified as IIa by mixed melting point with an authentic sample, yield 96%.

2-Chloro-1,3,2-benzoxathiarsole (IIb).

Method A.

A mixture of Ib (15) (10 mmoles), benzene (20 ml.) and arsenic trichloride (10 mmoles) was refluxed until the hydrogen chloride vapours completely disappeared. The solvent was then removed and the residue triturated with diisopropyl ether and filtered off to provide the product, yield 85%. An analytical sample was twice sublimed *in vacuo*, m.p. 65-67° [lit. (2) m.p. 94°].

Method B.

The same procedure as for IIa (Method B) was employed, starting from Ib (10 mmoles), benzene (10 ml.) and dichloroethoxyarsine (10 mmoles), yield 98%, m.p. 66-67°, spectral data (ir, nmr) were identical to the spectra of that product obtained from Method A.

2-(2'-Hydroxyphenyl)oxy-1,3,2-benzodioxarsole (IIIa).

A mixture of IIa (30 mmoles) and Ia (30 mmoles) was placed in an ampoule. The ampoule was sealed and heated in an oil bath at 150° for 48 hours. After cooling, the amber colored contents were crystallized from dichloromethane, yield 61%, m.p. 98-100°; ir: 3470, 3000, 1600, 1590, 1500, 1470, 1360, 1330, 1280, 1235, 1190, 1095, 1045, 1015, 930, 855, 800, 760, 745, 690, 645, 575, 565, 505, 450, 365, 355, 325, 305, 270, 210 cm⁻¹; nmr (deuteriochloroform): δ 7.00 (m, 8 H arom), and 5.40 ppm (s, 1 H, OH, deuterium oxide exchanged); ms: molecular ion, m/e 292 (Calcd. 292).

Anal. Calcd. for C₁₂H₉AsO₄: C, 49.34; H, 3.11; As, 25.64. Found: C, 49.17; H, 3.08; As, 25.51.

2-(2'-Hydroxyphenyl)thio-1,3,2-benzoxathiarsole (IIIb).

Method A.

Reaction of IIb (Method A), by evaporating the diisopropyl ether solution, gave a residue of crude IIIb. This was purified by eluting through a silica gel column using 1:1 mixture of petroleum ether-diethyl ether as eluent, to give a yellow oil; yield 10%; n_D²⁴ 1.6842; ir: 3400, 3040, 1610, 1570, 1560, 1450, 1430, 1280, 1260, 1230, 1140, 1120, 1055, 1015, 970, 920, 840, 750, 680, 650, 610, 560, 500, 455, 430, 400, 305, 290, 255, 210 cm⁻¹; nmr (deuteriochloroform): δ 6.90 (m, 8H arom) and 5.80 ppm (s, 1H, OH, deuterium oxide exchanged); ms: molecular ion, m/e 324 (Calcd. 324).

Anal. Calcd. for C₁₂H₉AsO₂S₂: C, 44.45; H, 2.80; As, 23.10; S, 19.78. Found: C, 44.28; H, 2.71; As, 22.95; S, 19.60.

Method B.

A mixture of IIb (50 mmoles) and Ib (50 mmoles) was heated, under nitrogen, at 150° in an oil bath until evolution of hydrogen chloride vapours ceased. After cooling the content was treated with hot dichloromethane and filtered. The dichloromethane solution was evaporated to give the product, yield 87%. Spectral data were identical to those of the product obtained from Method A.

2-(2'-Hydroxyphenyl)thio-1,3,2-benzodioxarsole (IIIc).

The same procedure as for IIb (Method B) was employed starting from IIa (30 mmoles) and Ib (30 mmoles), yield 93%. An analytical sample was obtained by microdistillation *in vacuo*; n_D²⁵ 1.6852; ir: 3470, 3040, 3010, 1600, 1570, 1470, 1450, 1340, 1300, 1240, 1220, 1190, 1160, 1130, 1030, 1005, 940, 830, 755, 695, 670, 650, 575, 485, 460, 435, 400, 340, 310, 290, 200 cm⁻¹; nmr (deuteriochloroform): δ 7.00 (m, 8 H arom) and 6.20 ppm (s, 1 H, OH, deuterium oxide exchanged); ms: molecular ion, m/e 308 (Calcd. 308).

Anal. Calcd. for C₁₂H₉AsO₃S: C, 46.77; H, 2.94; As, 24.31; S, 10.40. Found: C, 46.59; H, 2.81; As, 24.18; S, 10.27.

2-(2'-Hydroxyphenyl)oxy-1,3,2-benzoxathiarsole (III d).

This compound was obtained in the same manner described for IIIa starting from IIb (20 mmoles) and Ia (20 mmoles); yield 95%. An analytical sample was obtained by microdistillation *in vacuo*; n_D²⁴ 1.6827; ir: 3440, 3060, 1600, 1570, 1510, 1470, 1440, 1340, 1290, 1260, 1240, 1220, 1190, 1160, 1120, 1100, 1060, 1030, 1005, 930, 910, 840, 800, 745, 690, 645, 570, 490, 450, 430, 400, 370, 330, 310, 290, 210 cm⁻¹; nmr (deuteriochloroform): δ 7.15 (m, 8 H arom) and 6.40 ppm (s 1 H, OH, deuterium oxide exchanged); ms: molecular ion, m/e 308 (Calcd. 308).

Anal. Calcd. for C₁₂H₉AsO₃S: C, 46.77; H, 2.94; As, 24.31; S, 10.40. Found: C, 46.85; H, 2.87; As, 24.15; S, 10.23.

2,2'-[1,2-Phenylenebis(oxy)]bis-1,3,2-benzodioxarsole (IVa).

Method A.

A mixture of IIa (60 mmoles) and Ia (30 mmoles) was placed in a sealed ampoule and heated at 150° for 48 hours. After cooling, the content was poured into chloroform and filtered. The solvent was evaporated, the residue dissolved into dichloromethane and the solution treated with hexane to deposit a brown oil which was discarded. Evaporation of the solvent under reduced pressure afford practically pure IVa as white crystals; yield 43%, m.p. 114-115°; ir: 3010, 1595, 1510, 1475, 1410, 1335, 1230, 1150, 1095, 1030, 1010, 930, 855, 805, 760, 740, 690, 650, 575, 560, 440, 370, 330, 320, 210 cm⁻¹; the nmr spectrum (deuteriochloroform) consisted of aromatic signals at δ 7.05 ppm; ms: molecular ion, m/e 474 (Calcd. 474).

Anal. Calcd. for C₁₈H₁₂As₂O₆: C, 45.60; H, 2.55; As, 31.60. Found: C, 45.43; H, 2.48; As, 31.41.

Method B.

A mixture of IIIa (20 mmoles) and IIa (20 mmoles) was placed in a sealed ampoule and treated in the same manner above described. Yield 55%, m.p. 114-115° undepressed in admixture with a sample of product prepared under A.

2,2'-[1,2-Phenylene(oxy,thio)]bis-1,3,2-benzoxathiarsole (IVb).

Method A.

A mixture of IIb (60 mmoles) and Ib (30 mmoles) was placed

in a sealed ampoule and heated at 150° for 48 hours. After cooling, the content was poured into chloroform and filtered. The solvent was evaporated and the residue purified by washing four times with hot hexane. The product was obtained as yellow gum, yield 38%; ir: 3050, 2920, 1650, 1570, 1455, 1440, 1380, 1335, 1290, 1240, 1215, 1155, 1120, 1060, 1015, 930, 840, 785, 750, 710, 695, 650, 580, 500, 465, 440, 400, 335, 310, 270, 210 cm⁻¹; the nmr spectrum (deuteriochloroform) contained only aromatic signals at δ 6.95 ppm; ms: molecular ion *m/e* 522 (Calcd. 522).

Anal. Calcd. for C₁₈H₁₂As₂O₃S₃: C, 41.39; H, 2.32; As, 28.69; S, 18.41. Found: C, 41.15; H, 2.21; As, 28.48; S, 18.25.

Method B.

The same procedure as for IVa was employed starting from IIIb (20 mmoles) and IIb (20 mmoles); yield 59%. Spectral data were identical to the spectra of that product obtained from Method A. 2,2'-[1,2-Phenylenebis(oxy)]bis-1,3,2-benzoxathiarsole (IVc).

Method A.

A mixture of IIb (60 mmoles) and Ia (30 mmoles) was treated in the same manner described for IVb (Method A), to furnish the compound IVc as yellow gum, yield 38%; ir: 3050, 1980, 1925, 1645, 1570, 1455, 1440, 1385, 1330, 1290, 1260, 1240, 1220, 1155, 1120, 1100, 1060, 1015, 930, 900, 840, 805, 750, 715, 695, 650, 580, 500, 460, 440, 400, 350, 305, 270, 205 cm⁻¹; the nmr spectrum (deuteriochloroform) consisted of aromatic signals at δ 6.90 ppm; ms: molecular ion, *m/e* 506 (Calcd. 506).

Anal. Calcd. for C₁₈H₁₂As₂O₄S₂: C, 42.70; H, 2.39; As, 29.60; S, 12.67. Found: C, 42.43; H, 2.31; As, 29.38; S, 12.49.

Method B.

The same procedure as for IVa was employed starting from IIId (20 mmoles) and IIb (20 mmoles), yield 54%. The ir and nmr spectra of this material were identical with those of the product obtained from Method A.

2,2'-Spirobi[1,3,2-benzodioxarsole]-2-triethylamine (Va).

Method A.

To a stirred solution of IIa (10 mmoles) in anhydrous tetrahydrofuran (20 ml.) at room temperature a solution of Ia (10 mmoles), dry triethylamine (20 mmoles) and anhydrous tetrahydrofuran (10 ml.) was added dropwise under an atmosphere of nitrogen. The resulting mixture was stirred under reflux for six hours. The crude mixture of amine salt and product was chilled to 20° and poured into water; the insoluble fraction was collected, washed with hot tetrahydrofuran, air dried and recrystallized from water as white crystals, m.p. 113-115°; yield 90%; ir: 3030, 2980, 2960, 2820, 2680, 1580, 1480, 1400, 1330, 1270, 1260, 1240, 1200, 1100, 1030, 1010, 870, 800, 750, 650, 615, 600, 560, 535, 500, 460, 445, 370, 330, 310, 275, 240, 205 cm⁻¹; nmr (DMSO-d₆): δ 6.75 (m, 8 H arom), 3.00 (q, 6 H, CH₃-CH₂-) and 1.30 ppm (t, 9 H, CH₃-CH₂-); ms: 291 (M⁺ - Et₃N), 101 (Et₃N).

Anal. Calcd. for C₁₈H₂₃AsNO₄: C, 55.11; H, 5.91; As, 19.10; N, 3.57. Found: C, 54.97; H, 5.83; As, 18.96; N, 3.50.

Method B.

A mixture of IIa (5 mmoles) and dry triethylamine (20 ml.) was refluxed with stirring for five hours. After cooling, the reaction mixture was poured into water, filtered and worked up as in Method A, yield 45%. The compound isolated from this reaction was identical to an authentic sample obtained above (mixed m.p., ir and nmr data).

The aqueous solution was extracted repeatedly with diethyl ether; the ethereal extracts, dried on sodium sulphate and

analyzed by glc, showed a peak with the same retention time as Ia. Spiro [1,3,2-benzodioxarsole-2,2'-[1,3,2]-benzoxathiarsole]-2-triethylamine (Vb).

To a stirred solution of IIa (10 mmoles) in anhydrous tetrahydrofuran (20 ml.) at room temperature a solution of Ib (10 mmoles), dry triethylamine (20 mmoles) and anhydrous tetrahydrofuran (10 ml.) was added dropwise under an atmosphere of nitrogen. The reaction mixture was stirred under reflux for four hours and treated in the manner above described. The compound was obtained as white crystals, which were crystallized from water, yield 67%, m.p. 175-176°; ir: 3020, 2720, 1600, 1430, 1300, 1270, 1235, 1180, 1150, 1080, 1060, 1010, 860, 790, 750, 710, 680, 665, 650, 590, 570, 560, 545, 510, 490, 420, 400, 385, 345, 310, 275, 255, 230, 210 cm⁻¹; nmr (DMSO-d₆): δ 6.60 (m, 8 H arom), 3.00 (q, 6 H, CH₃-CH₂-) and 1.10 ppm (t, 9 H, CH₃-CH₂-); ms: 307 (M⁺ - Et₃N), 101 (Et₃N).

Anal. Calcd. for C₁₈H₂₃AsNO₃S: C, 52.94; H, 5.68; As, 18.34; N, 3.43; S, 7.85. Found: C, 52.78; H, 5.57; As, 18.20; N, 3.29; S, 7.69.

The same product Vb was obtained starting from IIb, Ia and triethylamine, yield 70%.

2,2'-Spirobi[1,3,2-benzoxathiarsole]-2-triethylamine (Vc).

Method A.

To a stirred solution of IIb (10 mmoles) in anhydrous tetrahydrofuran (20 ml.) at room temperature a solution of Ib (10 mmoles), dry triethylamine (20 mmoles) and anhydrous tetrahydrofuran (10 ml.) was added dropwise under an atmosphere of nitrogen. The reaction mixture was then treated in the same manner described for Va under A. The compound was obtained as white crystals, which were crystallized from water, yield 92%, m.p. 172-174°; ir: 3020, 2980, 2590, 1580, 1560, 1460, 1430, 1270, 1240, 1150, 1120, 1060, 1015, 840, 760, 740, 680, 645, 595, 570, 560, 545, 445, 415, 405, 385, 310, 275, 230, 210 cm⁻¹; nmr (DMSO-d₆): δ 6.60 (m, 8 H arom), 3.10 (q, 6 H, CH₃-CH₂-) and 1.20 ppm (t, 9 H, CH₃-CH₂-); ms: 323 (M⁺ - Et₃N), 101 (Et₃N).

Anal. Calcd. for C₁₈H₂₃AsNO₂S₂: C, 50.94; H, 5.46; As, 17.65; N, 3.30; S, 15.11. Found: C, 50.70; H, 5.40; As, 17.49; N, 3.21; S, 15.00.

Method B.

A mixture of IIa (5 mmoles) and dry triethylamine (20 ml.) was treated in the same manner described for Va under B, yield 41%. Spectral data (ir, nmr) were identical to the spectra of that product obtained from Method A and no depression was observed for a mixed melting point determination.

The aqueous solution was extracted with diethyl ether; the ethereal extracts, dried on sodium sulphate and analyzed by glc, showed a peak with the same retention time as Ib.

2-Hydroxy-1,3,2-benzodioxarsole (VIa).

A mixture of IIa (3 mmoles), water (5 ml.) and sodium hydroxide (3 mmoles) was kept with stirring for one hour at room temperature. Subsequently, the solution was extracted with chloroform. After drying over sodium sulphate, the solvent was evaporated and the practically pure compound crystallized as white crystals, yield 86%; m.p. 115-116°; ir: 3340, 3040, 1620, 1590, 1515, 1485, 1390, 1335, 1280, 1240, 1190, 1115, 1060, 1015, 935, 880, 860, 810, 750, 690, 650, 580, 565, 535, 420, 370, 355, 305, 280, 255, 225, 200 cm⁻¹; nmr (deuteriochloroform): δ 8.85 (s, 1 H, OH, deuterium oxide exchanged) and 6.80 ppm (m, 4 H arom); ms: molecular ion, *m/e* 200 (Calcd. 200).

Anal. Calcd. for C₆H₅AsO₃: C, 36.03; H, 2.52; As, 37.45.

Found: C, 35.65; H, 2.30; As, 37.15.

This compound, allowed to stand at room temperature, within a few hours gave, in almost quantitative yield, a white solid, which was identified as 2,2'-bi-(1,3,2-benzodioxarsole)oxide (Xa), m.p. 149-151° [lit. (13a) m.p. 150-150.5°].

2-Hydroxy-1,3,2-benzoxathiarsole (VIb).

A mixture of IIb (3 mmoles), water (5 ml.) and sodium hydroxide (3 mmoles) was worked up in the same manner described for the synthesis of VIa, giving a pale yellow oil; yield 70%; n_D^{28} 1.6225; ir: 3440, 3040, 2980, 2930, 2870, 1600, 1550, 1500, 1470, 1460, 1445, 1385, 1340, 1290, 1265, 1240, 1220, 1155, 1120, 1100, 1030, 1015, 930, 840, 750, 720, 685, 650, 570, 555, 490, 460, 430, 400, 365, 330, 300, 285, 265, 200 cm^{-1} ; nmr (deuteriochloroform): δ 7.15 (m, 4 H arom) and 6.30 ppm (s, 1 H, OH, deuterium oxide exchanged); ms: molecular ion, m/e 216 (Calcd. 216).

Anal. Calcd. for $\text{C}_6\text{H}_5\text{AsO}_2\text{S}$: C, 33.35; H, 2.33; As, 34.67; S, 14.84. Found: C, 33.12; H, 2.14; As, 34.50; S, 14.53.

This compound, within a few hours, furnished, in almost quantitative yield, a white solid, which was crystallized from benzene and identified as 2,2'-bi-(1,3,2-benzoxathiarsole)oxide (Xb), m.p. 67-68°; ir: 3040, 1570, 1460, 1440, 1265, 1230, 1120, 1060, 1015, 930, 840, 750, 720, 710, 695, 670, 650, 570, 480, 440, 400, 390, 345, 320, 300, 285, 265, 200 cm^{-1} ; the nmr spectrum (DMSO-d_6) contained only aromatic signals at δ 7.30 ppm; ms: molecular ion, m/e 414 (Calcd. 414).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{As}_2\text{O}_3\text{S}_2$: C, 34.80; H, 1.95; As, 36.18; S, 15.48. Found: C, 34.85; H, 2.09; As, 35.92; S, 15.25.

2-Ethoxy-1,3,2-benzodioxarsole (VIIa).

Method A.

Sodium ethoxide (2.5 mmoles) was added, under an atmosphere of nitrogen, to a stirred solution of IIa (2.5 mmoles) and dry benzene (50 ml.). The mixture was stirred at reflux for 12 hours, cooled, filtered and the solvent evaporated *in vacuo*. A pale yellow oil was obtained, yield 67%. An analytical sample was prepared by microdistillation *in vacuo*: n_D^{19} 1.5632; ir: 3040, 2910, 2830, 1600, 1470, 1350, 1325, 1275, 1240, 1180, 1150, 1100, 1030, 1015, 990, 950, 905, 870, 860, 800, 750, 695, 650, 575, 540, 445, 435, 400, 345, 320, 285, 265, 220 cm^{-1} ; nmr (deuteriochloroform): δ 6.90 (m, 4 H arom), 3.60 (q, 2 H, $\text{CH}_3\text{-CH}_2\text{-}$), and 1.10 ppm (t, 3 H, $\text{CH}_3\text{-CH}_2\text{-}$); ms: molecular ion, m/e 228 (Calcd. 228).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{AsO}_3$: C, 42.13; H, 3.98; As, 32.85. Found: C, 41.95; H, 3.81; As, 32.64.

Method B.

A mixture of Ia (50 mmoles) and triethoxyarsine (16) (50 mmoles) was kept at room temperature with stirring under a nitrogen atmosphere for 30 minutes. Ethanol was then distilled over *in vacuo* and the resultant pale yellow oil was identified as VIIa, yield 81%; the ir and nmr spectra of this material were identical with those of the product named above.

This compound, allowed to stand at room temperature, gave within a month, in almost quantitative yield, diethyl ether and Xa.

2-Ethoxy-1,3,2-benzoxathiarsole (VIIb).

Method A.

Sodium ethoxide (2.5 mmoles) was added, under an atmosphere of nitrogen, to a stirred solution of IIb (2.5 mmoles) and dry benzene (50 ml.). The resulting mixture was worked up in the same manner described for the synthesis of VIIa under A giving a pale yellow oil (94%), which was purified by microdistillation *in vacuo*; n_D^{19} 1.5848; ir: 3040, 2980, 2960, 1560, 1470, 1455, 1390, 1335, 1300, 1275, 1235, 1165, 1135, 1060, 1010, 930, 915, 845,

760, 735, 690, 650, 570, 480, 445, 435, 400, 375, 340, 310, 300, 285, 250, 200 cm^{-1} ; nmr (deuteriochloroform): δ 6.95 (m, 4 H arom), 3.45 (q, 2 H, $\text{CH}_3\text{-CH}_2\text{-}$) and 1.00 ppm (t, 3 H, $\text{CH}_3\text{-CH}_2\text{-}$); ms: molecular ion, m/e 244 (Calcd. 244).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{AsO}_2\text{S}$: C, 39.36; H, 3.72; As, 30.68; S, 13.13. Found: C, 39.14; H, 3.51; As, 30.40; S, 12.99.

Method B.

The same procedure as for VIIa under B was employed, starting from Ib (50 mmoles) and triethoxyarsine (50 mmoles), yield 90%. This material was identical to that prepared above.

The compound VIIb, allowed to stand at room temperature, gave within a month, in almost quantitative yield, diethyl ether and Xb.

2-p-Tolyloxy-1,3,2-benzodioxarsole (VIIIa).

Method A.

A mixture of IIa (30 mmoles), sodium *p*-cresolate (30 mmoles) and benzene (60 ml.) was worked up in the same manner described for the synthesis of VIIa under A giving a white solid, which was crystallized from benzene, yield 90%; m.p. 103-105°; ir: 3020, 2940, 2860, 1600, 1590, 1480, 1325, 1240, 1100, 1030, 1010, 990, 925, 855, 805, 760, 740, 695, 685, 650, 575, 565, 555, 435, 375, 365, 340, 320, 230 cm^{-1} ; nmr (deuteriochloroform): δ 6.95 (m, 8 H arom) and 2.30 ppm (s, 3 H, $\text{CH}_3\text{-}$); ms: molecular ion, m/e 290 (Calcd. 290).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{AsO}_3$: C, 53.81; H, 3.82; As, 25.82. Found: C, 53.54; H, 3.71; As, 25.55.

Method B.

A mixture of IIa (30 mmoles) and *p*-cresol (30 mmoles) was heated in oil bath at 150° until the hydrogen chloride vapours completely disappeared. After cooling, the precipitate was crystallized from benzene and identified as VIIIa by mixed melting point with an authentic sample and comparison of ir and nmr data, yield 65%.

This compound, allowed to stand at room temperature, gave within several months, in almost quantitative yield, *p*-tolyl ether and Xa.

2-p-Tolyloxy-1,3,2-benzoxathiarsole (VIIIb).

Method A.

This compound was obtained by a similar synthesis described for VIIIa under A, starting from IIb (30 mmoles), sodium *p*-cresolate (30 mmoles) and benzene (60 ml.), yield 95%; an analytical sample was prepared by microdistillation *in vacuo*: n_D^{29} 1.6380; ir: 3040, 2920, 2860, 1600, 1570, 1515, 1460, 1445, 1295, 1265, 1240, 1220, 1125, 1105, 1060, 1010, 930, 840, 820, 750, 715, 700, 680, 670, 650, 575, 540, 510, 460, 430, 400, 340, 310, 285, 200 cm^{-1} ; nmr (deuteriochloroform): δ 7.10 (m, 8 H arom) and 2.20 ppm (s, 3 H, $\text{CH}_3\text{-}$); ms: molecular ion, m/e 306 (Calcd. 306).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{AsO}_2\text{S}$: C, 50.99; H, 3.62; As, 24.46; S, 10.47. Found: C, 51.20; H, 3.75; As, 24.28; S, 10.30.

Method B.

The same procedure as for VIIIa under B was employed, starting from IIb (30 mmoles) and *p*-cresol (30 mmoles); yield 90%. This compound was identical in all respects with the above obtained product.

The compound VIIIb gave, within several months, in almost quantitative yield, *p*-tolyl ether and Xb.

2-p-Tolythio-1,3,2-benzodioxarsole (IXa).

Method A.

A mixture of IIa (30 mmoles), sodium *p*-toluenethiolate (30 mmoles) and benzene (60 ml.) was worked up in the same manner described for the synthesis of VIIIa, under A, giving a pale yellow oil which crystallized on standing, yield 92%. An analytical sample was prepared by microdistillation *in vacuo*; m.p. 33-34°; ir: 3020, 2910, 2860, 1595, 1470, 1395, 1320, 1300, 1235, 1210, 1175, 1115, 1095, 1080, 1035, 1015, 920, 850, 800, 745, 690, 650, 575, 565, 500, 490, 445, 395, 370, 330, 320, 290, 275, 200 cm⁻¹; nmr (deuteriochloroform): δ 7.10 (m, 8 H, arom) and 2.30 ppm (s, 3 H, CH₃-); ms: molecular ion, m/e 306 (Calcd. 306).

Anal. Calcd. for C₁₃H₁₁AsO₂S: C, 50.99; H, 3.62; As, 24.46; S, 10.47. Found: C, 50.78; H, 3.59; As, 24.25; S, 10.33.

Method B.

The same procedure for VIIIa under B was employed starting from IIa (30 mmoles) and *p*-toluenethiol (30 mmoles), yield 85%. Spectral comparison of IXa obtained from Methods A and B showed them to be identical.

2-*p*-Tolythio-1,3,2-benzoxathiarsole (IXb).

Method A

This compound was obtained as pale yellow oil from IIb (5 mmoles), sodium *p*-toluenethiolate (5 mmoles) and benzene (10 ml.) by the method described for VIIIa under A; yield 88%. An analytical sample was prepared by microdistillation *in vacuo*; n_D¹⁷ 1.6825; ir: 3070, 3030, 2980, 2940, 2920, 1600, 1575, 1490, 1460, 1445, 1400, 1380, 1340, 1305, 1295, 1265, 1240, 1225, 1180, 1160, 1120, 1080, 1030, 1015, 930, 910, 870, 840, 805, 750, 715, 700, 670, 650, 575, 485, 460, 435, 405, 340, 305, 290, 200 cm⁻¹; nmr (deuteriochloroform): δ 7.10 (m, 8 H arom) and 2.45 ppm (s, 3 H, CH₃-); ms: molecular ion, m/e 338 (Calcd. 338).

Anal. Calcd. for C₁₃H₁₁AsOS₂: C, 46.16; H, 3.28; As, 22.15; S, 18.96. Found: C, 45.99; H, 3.21; As, 21.95; S, 18.82.

Method B.

A mixture of IIb (10 mmoles) and *p*-toluenethiol (10 mmoles) was treated in the same manner described for VIIIa under B, to furnish the compound IXb, yield 78%; the ir and nmr spectra of this material were identical with those of the above obtained product.

2-*n*-Butyl-1,3,2-benzodioxarsole (XIa).

To a stirred solution of IIa (30 mmoles) in dry benzene (55 ml.) a solution of *n*-butyllithium in hexane (102 ml., 30 mmoles) was added dropwise under an atmosphere of nitrogen at room temperature. After additional stirring for four hours, the mixture was filtered and the solvent evaporated *in vacuo* to give a white oil, yield 81%. An analytical sample was prepared by microdistillation *in vacuo*; n_D²¹ 1.5070; ir: 2950, 2920, 2860, 1590, 1475, 1375, 1320, 1235, 1095, 1060, 1015, 945, 915, 885, 855, 800, 760, 750, 650, 570, 500, 465, 440, 410, 365, 350, 320, 290, 210 cm⁻¹; nmr (deuteriochloroform): δ 6.90 (m, 4 H arom), 1.40 (m, 6 H, three -CH₂- groups) and 0.90 ppm (t, 3 H, CH₃-); ms: molecular ion, m/e 240 (Calcd. 240).

Anal. Calcd. for C₁₀H₁₃AsO₂: C, 50.02; H, 5.46; As, 31.20. Found: C, 49.86; H, 5.38; As, 31.03.

The same product XIa was obtained performing the reaction at 80°.

2-*n*-Butyl-1,3,2-benzoxathiarsole (XIb).

This compound was prepared by a similar method described for XIa starting from IIb (30 mmoles), dry benzene (55 ml.) and *n*-butyllithium in hexane (102 ml., 30 mmoles), yield 78%. The analytical pure sample was obtained by microdistillation *in vacuo*; n_D¹⁹ 1.5861; ir: 2950, 2920, 2860, 1570, 1460, 1445, 1380, 1340, 1290, 1265, 1240, 1225, 1190, 1120, 1060, 1010, 970, 840, 750, 715, 690, 650, 570, 500, 460, 430, 395, 300, 285, 200 cm⁻¹; nmr (deuteriochloroform): δ 7.00 (m, 4 H arom), 1.45 (m, 6 H, three -CH₂-groups) and 0.90 ppm (t, 3 H, CH₃-); ms: molecular ion, m/e 256 (Calcd. 256).

Anal. Calcd. for C₁₀H₁₃AsOS: C, 46.88; H, 5.11; As, 29.24; S, 12.51. Found: C, 46.84; H, 5.18; As, 29.11; S, 12.34.

The same product XIb was obtained performing the reaction at 80°.

Acknowledgement.

Financial support from CNR (Rome) is gratefully acknowledged.

REFERENCES AND NOTES

- (1) C. Anchisi, S. Cabiddu, L. Corda, A. Maccioni and G. Podda, *J. Heterocyclic Chem.*, **13**, 1033 (1976).
- (2) K. Andra and L. Martschei, *Z. Anorg. Allg. Chem.*, **396**, 123 (1973).
- (3) Y. Yukawa, "Handbook of Organic Structural Analysis", W. A. Benjamin, Inc. New York, N.Y., 1965.
- (4) R. R. Shagidullin and T. E. Pavlova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2117 (1963); *Chem. Abstr.*, **60**, 11500f (1964).
- (5) R. R. Shagidullin and T. E. Pavlova, *ibid.*, 2091 (1966); *Chem. Abstr.*, **66**, 89819g (1967).
- (6) A. M. Sarquis and R. A. Zingaro, *J. Heterocyclic Chem.*, **10**, 909 (1973).
- (7) R. Burgada and C. Laurenço, *J. Organometal. Chem.*, **66**, 255 (1974).
- (8) A. B. Harvey and M. K. Wilson, *J. Chem. Phys.*, **44**, 3535 (1966).
- (9a) J. Kaufmann and F. Kober, *J. Organometal. Chem.*, **81**, 59 (1974); (b) O. Adler and F. Kober, *ibid.*, **72**, 351 (1974).
- (10) M. Wieber and N. Baumann, *Z. Anorg. Allg. Chem.*, **402**, 43 (1973).
- (11) K. A. Dari and J. V. Kingston, *Inorg. Nucl. Letters*, **10**, 1087 (1974).
- (12a) W. Schöniger, *Mikrochim. Acta*, 869 (1956); (b) H. Wagner, *ibid.*, 19 (1957); (c) M. Bigois, *Talanta*, **19**, 157 (1972).
- (13a) M. Eisenhut and R. Schmutzler, *Phosphorus*, **4**, 73 (1974); (b) H. Funk and H. Köhler, *J. Prakt. Chem.*, **13**, 324 (1961).
- (14) A. McKenzie and J. K. Wood, *J. Chem. Soc.*, 117, 406 (1920).
- (15) S. Cabiddu, A. Maccioni, M. Secci and V. Solinas, *Gazz. Chim. Ital.*, **99**, 397 (1969).
- (16) G. Kamai, *J. Gen. Chem. USSR*, **17**, 553 (1947); *Chem. Abstr.*, **42**, 860c (1948).