

Preparation of 1,3,2-Benzoxathiaphosphole, Arsole
and Stibole Derivatives by Exchange Methods

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A new convenient method for synthesis of heterocyclic compounds of five-membered rings containing an O-M-S (M = P, As, Sb) linkage is described. The compounds IIIa-c, IVa-b, Va-b, VI and VII were prepared starting from 2,2-dimethyl-1,3,2-benzoxathiastannole (II) and derivatives of phosphorus, arsenic and antimony. The structures of newly prepared compounds was determined by elemental analysis, spectroscopic methods (ir, nmr and ms) and comparison with authentic samples obtained *via* a different manner.

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The exchange reaction of the 2,2-dimethyl-1,3,2-benzodioxastannole with boron trichloride or dichloride derivatives and elements of the fifth main group has been reported previously (1).

In this work, 2,2-dimethyl-1,3,2-benzoxathiastannole (II) has been synthesized in good yields by the reaction of 2-hydroxythiophenol disodium salt I with dimethyltin dichloride. Analogously to 2,2-dimethyl-1,3,2-benzodioxastannole, this compound can be utilized in exchange reactions which allow the synthesis of heterocyclic derivatives containing O-M-S (M = P, As, Sb) linkages. The reactions which were investigated are summarized in Scheme 1. In all the cases, the heterocyclic compounds taken into consideration have been obtained in good yields and with a high degree of purity.

In a previous paper (2a,b) we reported the synthesis of derivatives IIIb, Vb, VI and VII, by the reaction of equimolar amounts of 2-hydroxythiophenol I with relative halides of arsenic and antimony, or nucleophilic substitution on the respective 2-chloro-1,3,2-benzoxathia-derivatives. The yields and the degree of purity of the compounds prepared in this manner are much lower than those obtained in the course of this work.

The synthesis of the compounds IIIa, IVa and Va was reported recently in the literature, by treating 2-hydroxythiophenol with phosphorus trichloride, dichlorophenylphosphine and dichloroethoxyphosphine, or by treating 2-chloro-1,3,2-benzoxathiaphosphole with sodium ethoxide or phenyllithium (3a-b). The corresponding chemical and physical properties of these latter compounds have not

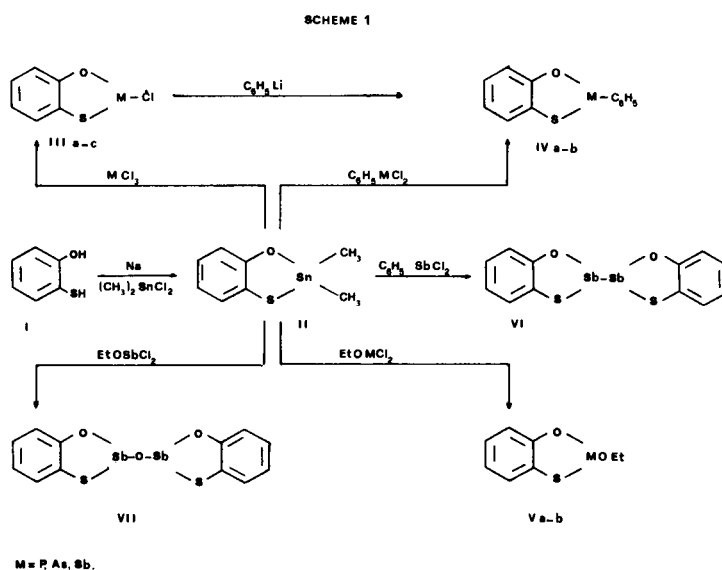


Table
Preparation of Heterocyclic Compounds of Five-Membered rings III_{a-c}, IV_{a-b}, V_{a-b}, VI and VII

Compound No.	Yield % (Literature Yield)	M.p. or n_D^t	Literature	Reference
IIIa	96 (93)	n_D^{21} 1,6631		3a
IIIb	97 (85)	m.p. 68-70°	65-67°	2b
IIIc	98 (80)	m.p. 185-187°	191°	2a
IVa	79 (a) 62 (b)	n_D^{23} 1,6585		
IVb	76 (a) 51 (b)	n_D^{22} 1,6878		
VI	82 (74)	m.p. 277°	275°	2a
Va	81 (-)	n_D^{23} 1,5268		3b
Vb	78 (94)	n_D^{16} 1,5735	n_D^{19} 1,5848	2b
VII	82 (67)	m.p. 279°	280°	2a

(a) Prepared by method A. (b) Prepared by method B.

been reported.

In this work the derivatives IIIa, IVa and Va were prepared, in good yields, by exchange reactions of II with phosphorus trichloride, dichlorophenylphosphine and dichloroethoxyphosphine, respectively. We have prepared the compound IVb, which was hitherto unknown, by two methods: (a) by the exchange reaction of II with dichlorophenylarsine; and (b) by reaction of equimolar amounts of 2-chloro-1,3,2-benzoxathiarsole IIIb, with phenyllithium in dry benzene. The structures of the compounds II and IV have been determined by elemental analysis and spectroscopic data. The analytical data for the derivatives obtained are reported in the Table.

EXPERIMENTAL

Literature procedures were followed in the preparation 2-hydroxythiophenol (4), phenyllithium (5), dichloroethoxyarsine (6), dichloroethoxyphosphine (7), dichloroethoxystibine (8), dichlorophenylarsine (9), and dichlorophenylstibine (10).

Melting points were determined on a Tottoli apparatus (uncorrected). Operations involved in the preparation were carried in an atmosphere of dry oxygen-free nitrogen.

Ir spectra were recorded on a Perkin-Elmer model 325 spectrophotometer; compounds were examined in the range of 4000-600 cm^{-1} using a pressed potassium bromide disk, and in the range of 700-200 cm^{-1} using nujol mulls between cesium iodide plates. Nmr spectra were taken using a Jeol-C-60 HL spectrometer; 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 were performed by the literature procedure (11).

2,2-Dimethyl-1,3,2-benzoxathiastannole (II).

To a stirred solution of I (30 mmoles) in dry benzene (75 ml.) and dry acetone (7.5 ml.), sodium (60 mmoles) was added under a nitrogen atmosphere to give a suspension of sodium 2-hydroxythiophenolate. The suspension was added to a solution

of dimethyltin dichloride (30 mmoles) in dry acetone (75 ml.) and stirred on a water-bath for several hours. The filtrate was evaporated under a reduced pressure. The residue obtained was triturated with ether and filtered off to provide the product, yield 70%, m.p. 205-206°, ir: 3040, 2920, 1580, 1460, 1440, 1270, 1240, 1215, 1125, 1060, 1035, 925, 840, 750, 715, 680, 600, 560, 540, 525, 515, 430, 390, 380, 250, 225 cm^{-1} ; nmr (deuteriochloroform): δ 1.18 (s, 6H, 2CH₃) and 6.91 ppm (m, 4H, arom.); ms: molecular ion, m/e 273 (Calcd. 273), 258 (loss of CH₃), 243 (loss of 2CH₃).

Anal. Calcd. for C₈H₁₀OSSn: C, 35.20; H, 3.69; S, 11.74. Found: C, 35.29; H, 3.71; S, 11.40.

2-Chloro-1,3,2-benzoxathiaphosphole (IIIa).

A mixture of II (30 mmoles) and phosphorus trichloride (30 mmoles) was heated, with stirring for half an hour at 150° under an atmosphere of nitrogen. Dimethyltin dichloride sublimed out of the reaction vessel leaving a crude reaction mixture, which was poured into benzene. The solvent was then removed in a rotary evaporator and the residue distilled under reduced pressure to give IIIa in almost quantitative yield; Pe/6 m = 98-100°, n_D^{21} = 1,6631; ir: 3060, 1580, 1460, 1445, 1265, 1200, 1120, 930, 870, 770, 750, 710, 690 cm^{-1} ; the nmr spectrum contained only aromatic signals at 7.00 ppm; ms: molecular ion, m/e 190 (Calcd. 190), 155 (loss of Cl).

Anal. Calcd. for C₆H₄ClOSP: C, 37.81; H, 2.11; S, 16.82. Found: C, 37.92; H, 2.31; S, 16.40.

Spectral data (ir and nmr) and elemental analyses were identical to those of the compound obtained by the literature procedure from I and phosphorus trichloride (3a). By this latter method, little quantities of the respective 2-(2'-hydroxyphenyl)-thio-1,3,2-benzoxathiaphosphole, together with compound IIIa were obtained.

2-Chloro-1,3,2-benzoxathiarsole (IIIb) and 2-Chloro-1,3,2-benzoxathiastibole (IIIc).

The same procedure as IIIa was employed starting from II (30 mmoles) and arsenic trichloride (30 mmoles) or antimony trichloride, respectively, to give IIIb and IIIc in quantitative yields.

The compound IIIb was recrystallized from diisopropyl ether and IIIc from benzene. Spectral data (ir, nmr) coincided well with those previously reported (2a,b).

2-Phenyl-1,3,2-benzoxathiaphosphole (IVa).

Method A.

This product was prepared as described above for IIIa starting from II (30 mmoles) and dichlorophenylphosphine (30 mmoles), yield 79%. An analytical sample was obtained by microdistillation *in vacuo*; $n_D^{23} = 1.6585$; ir: 3060, 3010, 1590, 1570, 1460, 1440, 1380, 1260, 1200, 1160, 1120, 1070, 1060, 1020, 930, 850, 760, 740, 700, 680 cm^{-1} ; the nmr spectrum (deuteriochloroform) consisted of aromatic signals at δ 7.40; ms: molecular ion, m/e 232 (Calcd. 232), 155 (loss of C_6H_5).

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{OSP}$: C, 62.06; H, 3.90; S, 13.80. Found: C, 61.87; H, 4.04; S, 13.92.

Method B.

To a stirred solution of 2-chloro-1,3,2-benzoxathiaphosphole (30 mmoles) in dry benzene (50 ml.), a solution of phenyllithium in benzene (30 mmoles) was added dropwise under an atmosphere of nitrogen at room temperature.

When the addition was completed the mixture was stirred under reflux for six hours. After cooling, the mixture was filtered and the solvent evaporated *in vacuo* to give a yellow oil, yield 62%. Spectral data (ir, nmr) were identical to the spectra of the product obtained from method A.

2-Phenyl-1,3,2-benzoxathiarsole (IVb).

Method A.

This compound was prepared by the same procedure described for IIIa starting from II (30 mmoles) and dichlorophenylarsine (30 mmoles), yield 76%.

The analytically pure sample was obtained by microdistillation *in vacuo*; $n_D^{22} = 1.6878$; ir: 3060, 1600, 1580, 1480, 1440, 1380, 1310, 1220, 1190, 1160, 1080, 1030, 1000, 920, 850, 740, 700, 670 cm^{-1} ; the nmr spectrum (deuteriochloroform) consisted of aromatic signals at δ 7.35 ppm; ms: molecular ion, m/e 276 (Calcd. 276), 199 (loss of C_6H_5).

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{AsOS}$: C, 52.18; H, 3.28; S, 11.60. Found: C, 52.50; H, 3.34; S, 11.33.

Method B.

To a stirred solution of 2-chloro-1,3,2-benzoxathiarsole (10 mmoles) in dry benzene (10 ml.), cooled to -10° , a solution of phenyllithium in dry benzene (7.5 ml., 10 mmoles) was added dropwise under an atmosphere of nitrogen. After slowly warming to room temperature, the mixture was filtered and the solvent evaporated *in vacuo* to give a yellow oil, yield 51%. The ir and nmr spectra of this material were identical with those of the product obtained from method A.

2,2'-Bi(1,3,2-benzoxathiaistibole) (VI).

The same procedure used for IIIa was employed starting from II (30 mmoles) and dichlorophenylstibine (30 mmoles), yield 82%. The spectral data of this material coincided well with those of an authentic sample obtained by literature procedures (2a).

2-Ethoxy-1,3,2-benzoxathiaphosphole (Va).

This product was prepared as described above for IIIa,

starting from II (30 mmoles) and dichloroethoxyphosphine (30 mmoles), yield 81%. An analytical sample was prepared by microdistillation *in vacuo*; $n_D^{23} = 1.5268$; ir: 3040, 2980, 2920, 2860, 1580, 1460, 1370, 1250, 1230, 1165, 1090, 1030, 980, 820, 800, 750, 670 cm^{-1} ; nmr (deuteriochloroform): δ 7.3 (m, 4H arom.), 4.3 (q, 2H, CH_3CH_2) and 1.3 ppm (t, 3H, $\text{CH}_3\text{-CH}_2$); ms: molecular ion, m/e 200 (Calcd. 200), 155 (loss of OC_2H_5).

Anal. Calcd. for $\text{C}_8\text{H}_9\text{O}_2\text{SP}$: C, 47.99; H, 4.53; S, 16.01. Found: C, 48.26; H, 4.31; S, 15.87.

Spectral data (ir and nmr) and elemental analyses were identical to those obtained for compound synthesized by the literature procedure starting from IIIa and sodium ethoxide (3b).
2-Ethoxy-1,3,2-benzoxathiarsole (Vb).

This compound was prepared by a similar method described for IIIa, starting from II (30 mmoles) and dichloroethoxyarsine (30 mmoles), yield 78%. The ir and nmr spectra coincided well with those previously reported (2b).

2,2'-Bis(1,3,2-benzoxathiaistibole)oxide (VII).

A mixture of II (30 mmoles) and dichloroethoxystibine (30 mmoles) was treated in the same manner described for IIIa, gave compound VII, yield 82%. The ir and nmr spectra of this material were identical with those of the product obtained by literature procedures (2a).

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