Studies on the Synthesis of Heterocyclic Compounds. VII. Action of Acyl Halides on Heterocyclic Compounds Containing the O-M-O (M = P, As, Sb) Bond in the Ring

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The action of acyl halides on heterocyclic compounds of five-membered rings containing an O-M-O (M = P, As, Sb) linkage is described. The reactions were either carried out in the presence of a solvent (benzene or toluene) or by direct heating of the reagent with the substrate. In the case of arsole, stibole and stannole derivatives, the cleavage of O-M bond and the formation of the respective mono- and diesters were always obtained, while with the phospholes, no cleavage of the compounds was observed.The products IIa-c (M = Sb) have been obtained in excellent yields starting from VIa-c and antimony trichloride. The structure of the compounds which were prepared was determined by analytical and spectroscopic methods and also by comparations with authentic samples where possible.

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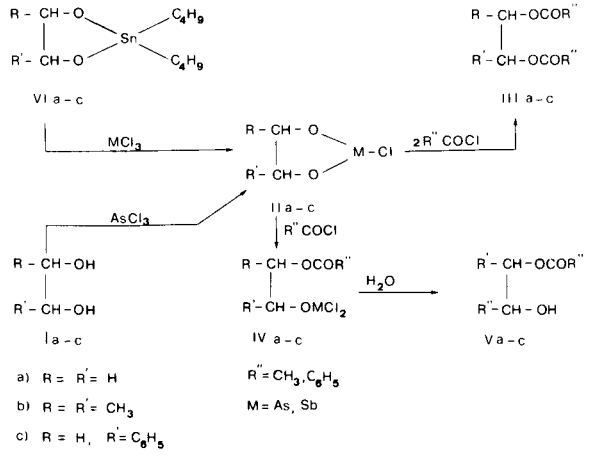
In the preceding papers we investigated and synthesized arsenic and antimony heterocyclic benzo-condensed derivatives *via* the condensation of 1,2-benzenediols or 2-hydroxythiophenols with arsenic and antimony trichloride or dichloride derivatives (1a,b) or *via* an exchange reaction of 2,2-dimethyl-1,3,2-benzodioxa- or benzoxathiastannole with the same halides (2a,b). Subsequently, the research work was extended to the synthesis of 2-substituted 1,2,3-dioxaphosphole and arsole derivatives by the exchange reaction starting from 2,2-di-*n*-butyl-1,3,2-dioxastannole and tri or dihalides of phosphorus and arsenic (3).

The 2-chloro-1,3,2-dioxarsole derivatives IIa-c (M = As) were prepared by the condensation reaction of the respective diols Ia-c with arsenic trichloride in the presence of triethylamine or pyridine in dry diethyl ether (4a,b) or by the exchange reaction of 2,2-di-*n*-butyl-1,3,2-dioxastannoles VIa-c with the same halide (3). The analogous derivatives IIa-c (M = Sb) have only been synthesized by the exchange reaction between antimony trichloride and the corresponding stannoles (Scheme 1) since treatment of the diols with antimony trichloride by refluxing in benzene or toluene reacted slowly and gave low yields.

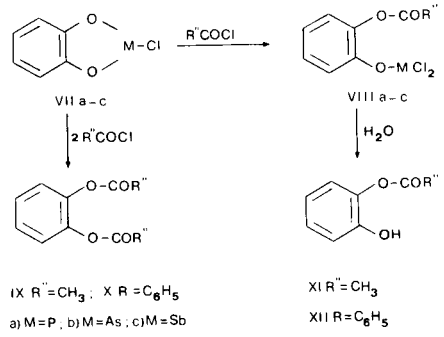
Scheme 1



We now report the protocal for the synthesis of mono and diesters which are obtained by action of acyl halides on compounds containing the O-M-O (M = P, As. Sb) linkage of the type reported above. The synthesis of the mono products from difunctional substrates is a general problem. In the field of the symmetrical diol substrates, Leznoff, *et al.*, (5a,b) resolved the problem using polymer support reagents and more recently Shanzer (6) obtained excellent results by transformation of diols into stannoles and subsequently into the desired monoesters and the symmertrical and non-symmetrical diesters.

By reaction of 2-chloro-1,3,2-dioxarsoles and -dioxastiboles IIa-c with two equivalent of acetyl or benzoyl chloride, we obtained the corresponding diesters IIIa-c in high yields with the simultaneous formation of arsenic or antimony trichloride. Probably, the acyl halide initially causes a cleavage of the O-M bond giving the monoesters of the intermediate diols IVa-c, which are successively attacked by a second mole of acyl halide forming the symmetrical diesters IIIa-c. Repeating the reaction between the same compounds IIa-c and acyl halides in the molar ratio of 1:1, after hydrolysis, the corresponding monoesters Va-c were obtained. Analogously, by allowing 2-chloro-1,3,2-benzodioxarsoles VIIb and -stiboles VIIc to react with acyl halides, the corresponding monoesters XI, XII and diesters IX, X were prepared (Scheme 2). The

Scheme 2



yields of the diesters of catechol obtained from the reaction of 2-chloro-1,3,2-benzodioxastiboles VIIc and acyl halides were quantitative either in absence or in the presence of solvent (benzene or toluene).

Starting from VIIb and two equivalent of acyl halide in the absence of solvent, the diesters were obtained in quantitative yields while in the presence of solvent a mixture of mono- and diesters was always obtained. The amount of monoester increases up to 20% of the total yield upon dilution. The reaction of compound VIIa with an excess of acyl halide by heating in reflux for several hours gave no cleavage material. The starting compound was always recovered. This behaviour was in agreement with the values of the O-M bond energy which decreases from phosphorus to antimony.

Mono- and diesterification reactions of catechol were also repeated starting from 2,2-di-*n*-butyl-1,3,2-benzodioxastannoles and acyl halides in a molar ratio 1:1 and 1:2, respectively. Furthermore, in this case the desired esters were obtained in excellent yields.

The structure of the compounds here described have been assigned on the basis of their analytical, physical and spectral data. Data concerning elemental analyses, ir, nmr and ms spectra are reported in the Experimental.

EXPERIMENTAL

Literature procedures were followed in the preparation 2-chloro-1,3,2-dioxarsole (4a,b), 2-chloro-4,5-dimethyll,3,2-dioxarsole (4a,b), 2-chloro-4-phenyl-1,3,2-dioxarsole (3), 2,2-dibutyl-1,3,2,-dioxastannole (7a,b), 2,2-dibutyl-4,5-dioxastannole (7a,b), 2,2-dibuthyl-4-phenyl-1,3,2-dioxastannole (3), 2-chloro-1,3,2-benzodioxaphosphole (2a,8),2-chloro-1,3,2-benzodioxarsole (1b,2a) and 2-chloro-1,3,2-benzodioxastibole (1a,2a).

Melting points were determined on a Tottoli apparatus and are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Model 325 spectrophotometer. Absorption frequencies are quoted in reciprocal centimeters; samples were examined as potassium bromide pellets or as thin films in the case of liquids. The nmr spectra were determined on a Varian FT-80A spectrometer; chemical shifts were measured in ppm (δ) using tetramethylsilane as an internal reference. The mass spectra were determined on a Hitachi Perkin-Elmer RMU-6D spectometer at 70 eV. Microanalyses for CHN were carried out on a Perkin-Elmer model 240 elemental analyzer. All products were identified by analytical and spectroscopic data or by comparison with authentic samples. The preparation of the compounds is described below using general procedures where possible.

General Procedure for the Preparation of IIa-c (M = Sb).

To a heated solution of VIa-c in benzene, antimony trichloride was added with stirring. When the addition was completed, the reaction mixture was refluxed for approximately four hours. The white precipitate was filtered, washed with hot benzene and purified. After drying the compounds were identified as IIa-c (M = Sb). The benzene solution was then removed using a rotary evaporator to give a white solid identified as dibutyltin dichloride, mp 38° (lit (9) mp 42°).

Using this general procedure, the following compounds were prepared.

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

From the reaction of 2,2-dibutyl-1,3,2-dioxastannole (VIa) (13.8 mmoles) with 20 ml of benzene and antimony trichloride (13.8 mmoles), a white precipitate was obtained which was purified from hot benzene giving IIa, yield 96%, mp 228-230° dec; ir: 2920, 2860, 1440, 1340, 1250, 1140, 920, 870, 720 cm^{-1}; nmr (DMSO-d_6): δ 3.40 ppm (s, 4H, CH_2-O); ms: molecular ion, m/e 217 (Calcd. 217).

*Anal.*Calcd. for $C_2H_4ClO_2Sb$: C, 11.05; H, 1.84; Cl, 16.32. Found: C, 11.01; H, 1.80; Cl, 16.28.

2-Chloro-4,5-dimethyl-1,3,2-dioxastibole (IIb).

The reaction of 2,2-dibutyl-4,5-dimethyl-1,3,2-dioxastannole VIb (9.3 mmoles) with 20 ml of benzene and antimony trichloride (9.3 mmoles) gave IIb as a white solid, yield 88%, mp 270-273% dec; ir: 2960, 2880, 1440, 1340, 1250, 1140, 1050, 920, 870, 720, cm^{-1}; nmr (DMSO-d_6): δ 3.40 (m, 2H, CH_3-C*H*-O) and 0.92 ppm (d, 6H, C*H*$_3$-CH-O); ms: molecular ion, m/e 245 (Calcd. 245).

Anal. Calcd. for $C_4H_8ClO_2Sb$: C, 19.59; H, 3.26; Cl, 14.45. Found: C, 19.51; H, 3.24; Cl, 14.38.

2-Chloro-4-phenyl-1,3,2-dioxastibole (IIc).

From 2,2-dibutyl-4-phenyl-1,3,2-dioxastannole VIc (8 mmoles), 20 ml of benzene and antimony trichloride (8 mmoles) IIc was obtained, yield 85%, mp 238-240° dec; ir: 3040, 2920, 2850, 1600, 1450, 1340, 1310, 1270, 1230, 1200, 1170, 1090, 1040, 1000, 910, 830, 760, 700, 650, cm^{-1}; nmr (DMSO-d_6): δ 7.30 (m, 5H, arom.), 4.2 (m, 1H, C_6H_5-C*H*-CH_2-O) and 3.56 ppm (m, 2H, CH_2-O); ms: molecular ion, m/e 293 (Calcd. 293).

*Anal.*Calcd. for $C_8H_8ClO_2Sb$: C, 32.75; H, 2.72; Cl, 12.09. Found: C, 32.84; H, 2.73; Cl, 12.05.

General Procedures for the Preparation of Mono and Diesters.

A stirred mixture of IIa-c (M = As, Sb) and acetyl or benzoyl chloride was heated under reflux for several hours. At the end of the reaction period, the mixture was allowed to cool to room temperature and purified by recrystallization or by distillation under reduced pressure or by column chromatography on silica gel.

Using this general procedure, the following compounds were prepared.

Glycol Diacetate (IIIa, R'' = CH_3).

A mixture of IIa (M = As, Sb) (30 mmoles) and acetyl chloride (65 mmoles) was heated for several hours. The reaction mixture was distilled under reduced pressure to give IIIa in quantitative yield, bp 69-71° (10 mm); n_D^{25} 1,4150 (lit (10) bp 186-187° (760 mm); n_D^{15} 1,4183).

The ir and nmr spectra and elemental analyses of this compound were identical with those of the product obtained by the literature procedure (10).

Glycol Dibenzoate (IIIa, R'' = C_6H_5), 2,3-Dimethylglycol Diacetate (IIIb, R'' = CH_3) and 2,3-Dimethylglycol Dibenzoate (IIIb, R'' = C_6H_5).

The same procedure was employed for the glycol diacetate IIIa starting from IIa-b (30 mmoles) and acetyl chloride (65 mmoles) or benzoyl chloride (65 mmoles) respectively, to give IIIa-b in quantitative yields. Spectral data (ir, nmr) coincided well with those previously reported (11,12a-b).

2-Phenylglycol Diacetate (IIIc, R'' = CH_3).

Method A.

This product was prepared as described for IIIa, starting with IIc, (M = As, Sb) (30 mmoles) and acetyl chloride (65 mmoles) to give IIIc in quantitative yield, bp 146° (10 mm), n_D^{18} 1.5121; ir: 3040, 2940, 2920, 2850, 1720, 1600, 1450, 1370. 1225, 1080, 1050, 950, 880, 760, 700, cm^{-1}; nmr (deuteriochloroform); δ 7.35 (m, 5H, arom.), 6.00 (t, 1H, -C*H*-O-), 4.34 (d, 2H, CH_2-O), 2.11 (s, 3H, C*H*$_3$), 2.04 ppm(s, 3H, C*H*$_3$); ms: molecular ion, m/e 222 (Calcd. 222).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.93; H, 6.37.

Method B.

A mixture of Ic (50 mmoles), acetyl chloride (115 mmoles) and triethylamine (115 mmoles) was stirred for one day at room temperature. After the mixture was fractionally distilled under reduced pressure, the yield was 81% of IIIc as a pale yellow liquid. Spectral data (ir, nmr and ms) and elemental anayses of this compound were identical to those of the product obtained from method A.

2-Phenylglycol Dibenzoate (IIIc, R'' = C_6H_5).

Method A.

This compound was prepared by the same procedure described for IIIa starting from IIc (30 mmoles) and benzoyl chloride (65 mmoles). The mixture was recrystallized from petroleum ether 40-70° giving IIIc in quantitative yield, mp 84-85°; ir: 3040, 2910, 2850, 1700, 1600, 1490, 1450, 1430, 1320, 1250, 1200, 1170, 1100, 1070, 1020, 980, 920, 890, 860, 800, 760, 740, 700 cm^{-1}; nmr (deuteriochloroform): δ 8.03-7.47 (m, 15H, arom.), 6.44 (t, 1H, C*H*-O), 4.66 ppm (d, 2H, CH_2-O); ms: molecular ion, m/e 346 (Calcd. 346).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.33; H, 5.26.

Method B.

Analogously to method B, described for 2-phenylglycol diacetate, IIIc was prepared starting from phenylethylenglycol, benzoyl chloride and triethylamine, yield 90%, mp 84°, unaltered by mixed mp with a sample obtained by method A. Spectral data (ir, nmr and ms) and elemental analyses were identical with those of the product obtained from method A.

Glycol Monoacetate (Va, R'' = CH_3).

A solution of IIa (M = As, Sb) (30 mmoles) and acetyl chloride (30 mmoles) was heated for several hours. After cooling, the reaction mixture was poured into water and extracted with chloroform (3 × 15 ml). The organic layer was dried with sodium sulfate and evaporated to give crude Va. The product on distillation afforded a quantitative yield of Va, bp 81-82° (13 mm) (lit (13) bp 80-81° (12 mm). The ir and nmr spectra and elemental analyses of this compound were identical with those of the product obtained by the literature procedure (13).

Glycol Monobenzoate (Va, R'' = C_6H_5), 2,3-Dimethylglycol Monoacetate (Vb, R'' = CH_3) 2,3-Dimethylglycol Monobenzoate (Vb, R'' = C_6H_5).

Those compounds were obtained in the same manner described for Va, starting from IIa-b (30 mmoles) and acetyl or benzoyl chloride (30 mmoles) to give Va-b. Spectral data (ir, nmr) and elemental analyses coincided well with those of authentic samples obtained by literature procedures (11,14).

2-Phenylglycol Monoacetate (Vc, R'' = CH_3).

Method A.

This product was prepared as described above for Va starting with IIc (M = As, Sb) (30 mmoles) and acetyl chloride (30 mmoles), yield 82%. An analitical sample was obtained by microdistillation *in vacuo* as a colourless viscous liqiud which, after cooling in a freezer, gave white plates, mp 56-57°; ir: 3390. 3070, 3040, 2950, 2880, 1740, 1600, 1490, 1460, 1380, 1320, 1240, 1040, 980, 920, 890, 760, 700 cm^{-1}; nmr (deuteriochloroform): δ: 7.30 (m, 5H, arom.), 5.90 (t, 1H, -C*H*-O-), 4.24 (d, 2H, CH_2-O-), 2.60 (s, 1H, OH, deuterium oxide exchanged), 2.08 ppm (s, 3H, CH_3).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.93; H, 6.73.

Method B.

This compound was prepared by the same procedure described for IIIc (method B), starting from Ic (30 mmoles), acetyl chloride (30 mmoles) and triethylamine (30 mmoles), yield 78%, mp 55°. The mixture mp with the sample isolate by method A was unaltered and the ir and nmr spectra were identical.

2-Phenylglycol Monobenzoate (Vc, R'' = C_6H_5).

Method A.

Analogously to the method described for 2-phenylglycol monoacetate Vc, was prepared 2-phenylglycol monobenzoate in quantitative yield. An analytical sample was obtained by microdistillation *in vacuo* as a colourless viscous liquid which, after cooling in the freezer, gave white plates, mp 48-50°; ir: 3400, 3070, 3040, 2950, 1740, 1600, 1580, 1490, 1380, 1320, 1270, 1180, 1120, 1100, 1070, 1030, 980, 910, 850, 800, 760, 700 cm^{-1}; nmr (deuteriochlorform): δ 8.00-7.42 (m, 10H, arom.), 5.92 (t, 1H, C*H*-O), 4.51 (d, 5H, CH_2-O), 2.80 ppm (s, 1H, OH, deuterium oxide exchanged).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.23; H, 5.81.

Method B

Analogously to method B, described for Vc was prepared 2-phenylglycol monobenzoate Vc, yield 81%, mp 47-48°; unaltered by a mixed mp with the sample isolated by method A. Spectral data (ir and nmr) and elemental analyses were identical with those of the product obtained from method A.

Reaction of 2-Chloro-1,3,2-benzodioxaphosphole (VIIa) with an Excess of Acetyl of Benzoyl Chloride in Benzene or Without Solvent.

A mixture of VIIa (60 mmoles) and acetyl chloride (130 mmoles) in dry benzene (or without solvent) was refluxed with stirring for serveral hours. After cooling, the mixture was distilled under reduced pressure and the compound was identified as starting materials.

Reaction of 2-Chloro-1,3,2-benzodioxarsole (VIIb) or 2-Chloro-1,3,2-benzodioxastibole (VIIc).

a) With an Excess of Acetyl Chloride.

A mixture of VIIb or VIIc (30 mmoles) and acetyl chloride (65 mmoles) was heated to reflux with stirring for 0.5 hour. After cooling to room temperature, the reaction mixture was crystallized from ethanol to give pure IX as a white solid in almost quantitative yield, mp 64-65° (lit (15a,b) mp 64°.) The spectral data (ir and nmr) of this material coincided well with those of an authentic sample obtained by literature procedures (15a,b).

b) With an Excess of Benzoyl Chloride.

A mixture of compound VIIb or VIIc (30 mmoles) and benzoyl chloride (65 mmoles) was treated as described above to give X in quantitative yield which on crystallization from ethanol melted 83-84° (lit (16) mp 84°). The ir and nmr spectra coincided well with those previously reported (16).

c) With an Excess of Acetyl or Benzoyl Chloride in Benzene.

The reaction of VIIb (30 mmoles) in dry benzene (10 ml) and acetyl or benzoyl chloride (65 mmoles) gave a mixture of IX and XI or X and XII in yield of 65% (IX,X) and 20% (XI, XII) respectively, while the reaction of VIIc (30 mmoles) and acetyl or benzoyl chloride (65 mmoles) in dry benzene (10 ml) gave IX or X in quantitative yield.

d) With Equimolar Amounts of Acetyl Chloride

A mixture of VIIb or VIIc (30 mmoles) and acetyl chloride (30 mmoles) was heated to reflux with stirring for 0.5 hour. After cooling, the mixture was purified by chromatography on a silica gel column using petroleum ether 40-70° and diethyl ether (2:1) as eluent and was identified as XI in quantitative yield. An analytical sample was obtained by microdistillation *in vacuo* as a viscous liquid, which, after cooling in the freezer, gave white plates, mp 55° (lit (15a) mp 57-58°); ir: 3460, 2920, 2840, 1760, 1600, 1490, 1460, 1370, 1240, 1200, 1160, 1100, 1030, 1010, 940, 910, 850, 830, 800, 750, cm^{-1}; nmr (deuteriochloroform): δ 7.24-6.77 (m, 4H,

arom.), 6.05 (s, 1H, OH, deuterium oxide exchanged, 2.27 ppm (s, 3H, COO-CH_3).

Anal. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30 Found: C, 63.10; H, 5.28.

e) With Equimolar Amounts of Benzoyl Chloride.

A mixture of compound VIIb or VIIc (30 mmoles) and benzoyl chloride was treated as descibed above for "d" to give XII in almost quantitative yield, mp 130° (lit (17) mp 130-131°); ir: 3440, 3060, 1740, 1600, 1490, 1450, 1320, 1270, 1240, 1170, 1100, 1080, 1060, 1020, 850, 800, 750, 700 cm^{-1}; nmr (deuteriochloroform): δ 8.02-7.40 (m, 9H, arom.), 7.25 ppm (s, 1H, OH, deuterium oxide exchange).

Anal. Calcd. for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.56; H, 4.73.

f) With Equimolar Amounts of Acetyl or Benzoyl Chloride in Dry Benzene.

When the same reaction between VIIb or VIIc (30 mmoles) and acetyl or benzoyl chloride (30 mmoles) was carried out in dry benzene at reflux for several hours a mixture of IX and XI or X and XII was obtained in lower yield. Compounds were purified by chromatography on a silica gel column using petroleum ether 40-70° and diethyl ether (2:1) as eluent. The spectral data (ir and nmr) and elemental analyses coincided well with those of authentic sample obtained be literature. (15a,b-18).

Reaction Between 2,2-Di-*n*-butyl-1,3,2-benzodioxastannole and Acetyl or Benzoyl Chloride.

The reaction of 2,2-di-*n*-butyl-1,3,2-benzodioxastannole and acetyl chloride or benzoyl chloride in dry benzene (or without solvent) in a molar ratio of 1:2 or 1:1 gave the compounds IX or X, XI or XII in quantitative yield. Spectral data were identical to those of products obtained by literature procedures (15 a,b-18).

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