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SOME *N*-TRIARYLTIN AND -LEAD DERIVATIVES OF CERTAIN PURINES

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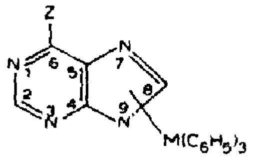
Hydrolytically stable triorganotin[1,2] and -lead[3] compounds in which the tin or lead atom is bonded to nitrogen in imidazole, 1,2,3- and 1,2,4-triazole, and condensed imidazoles and triazoles have been prepared by allowing the appropriate heterocyclic compound to react with a bis(triorganotin) oxide or triorganolead hydroxide.

We wish to report that hydrolytically stable *N*-triphenylstannyl and -plumbyl derivatives of purine, 6-chloropurine, and 6-methylmercaptopurine (I) can be prepared in good yield by allowing the purine compound to react with bis(triphenyltin) oxide or triphenyllead hydroxide in refluxing acetone. The structures (I) are supported by the elemental analyses and also, by the infrared data. Purine is reported[4] to exhibit a broad hydrogen bonded NH stretching frequency between 2900 and 2400 cm^{-1}. This band was observed at about 2762 cm^{-1} for purine, 2770 cm^{-1} for 6-chloropurine, and 2770 cm^{-1} for 6-methylmercaptopurine. The absence of an absorption band in this region for the compounds (I) provides further support for the formation of the tin–nitrogen or lead–nitrogen bond. Another major characteristic of the infrared spectrum of each of these compounds was the presence of two bands at about 730 cm^{-1} and 698 cm^{-1} attributable to monosubstituted benzene[5]. The position of the triphenyltin or -lead group cannot be deduced from the present data. However, since methylation of purine with dimethyl sulfate or methanolic diazomethane occurs exclusively at the N-9 position[6], it is likely that the tin or lead atom in our compounds is also attached to N-9.

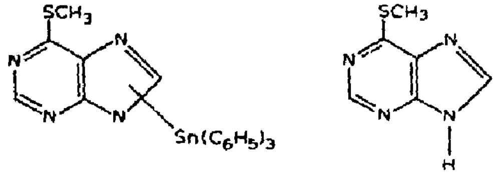


$Z = H$; $M = Sn$ or Pb
$Z = Cl$; $M = Sn$ or Pb
$Z = SCH_3$; $M = Pb$

(I)

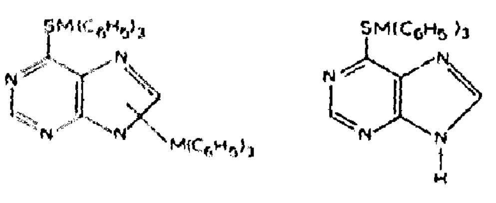
The compounds (I) were stable to the moisture in the air and no special precautions were required for their handling. In several cases water was added to the reaction mixture to cause precipitation of the product; furthermore, *N*-(triphenylplumbyl)-6-methylmercaptopurine was recrystallized from acetonitrile/water.

The reaction of 6-methylmercaptopurine with bis(triphenyltin) oxide did not give the expected *N*-(triphenylstannyl)-6-methylmercaptopurine. On the basis of elemental analysis, the product (94% yield) was assigned structure (II). A further distinction between (II) and *N*-(triphenylstannyl)-6-methylmercaptopurine was provided by a careful study of the stoichiometry of the reaction. For example, the reaction of 6-methylmercaptopurine (0.008 mole) with bis(triphenyltin) oxide (0.002 mole) could have afforded either 2.73 g of (II) or 2.06 g of *N*-(triphenylstannyl)-6-methylmercaptopurine plus unreacted 6-methylmercaptopurine. The sole product isolated (2.56 g) represented a 94% yield of (II). The infrared spectrum of (II) had absorption bands at 730 cm^{-1} and 695 cm^{-1} characteristic of monosubstituted benzene[5]. The NH absorption band observed at 2770 cm^{-1} in the infrared spectrum of 6-methylmercaptopurine appeared to be absent (or at least greatly diminished in intensity) in the spectrum of (II). The NMR spectrum of (II) showed a singlet at 2.62 ppm, a complex multiplet at 7.20 to 8.30 ppm, and a singlet at 8.56 ppm. The integration of the high field singlet indicated the presence of six equivalent methyl protons. The equivalency of the two methyl groups suggests that the 6-methylmercaptopurine moiety in (II) is probably attached to tin through a nitrogen atom rather than through a sulfur atom. The integration of the multiplet indicated the presence of eighteen protons representing two purine ring protons, probably at C-8, one NH proton, and fifteen aromatic protons due to the three phenyl groups. The low field singlet is believed to represent two purine ring protons at C-2[7]. Upon addition of D_2O to the sample solution the NH proton from the complex band was lost through exchange and an HDO band appeared at 3.95 ppm.



(II)

The reaction of 6-mercaptopurine monohydrate with either bis(triphenyltin) oxide or triphenyllead hydroxide gave products which were assigned, on the basis of the elemental analyses, structure (III). A careful study of the stoichiometry of the reactions provided support for the assigned structures. For example, the reaction of 6-mercaptopurine monohydrate (0.04 mole) with bis(triphenyltin) oxide (0.03 mole) could have afforded one of the following: 27.0 g of (III), 20.0 g of 6-(triphenylstannyl)-mercaptopurine plus unreacted 6-mercaptopurine monohydrate or 25.7 g of *N*-(triphenylstannyl)-6-(triphenylstannyl)mercaptopurine plus unreacted 6-mercaptopurine monohydrate. The amount of product isolated (26.32 g) represented a 97% yield



(III, M = Sn or Pb)

of (III). 6-(Triphenylstannyl)mercaptopurine was also eliminated by the fact that the product did not react with an 8 *M* excess of bis(triphenyltin) oxide. (III) was always obtained irrespective of the molar ratio of 6-mercaptopurine monohydrate/bis(triphenyltin) oxide used; when the molar ratio was 1/1 the yield was 92%.

The infrared spectrum of 6-mercaptopurine monohydrate showed a strong band at 2778 cm^{-1} due[8] to hydrogen bonded NH. In the infrared spectrum of (III) this band appeared to be absent (or at least greatly diminished in intensity). (III) possessed the expected bands due to monosubstituted benzene at 731, 698 cm^{-1} (M = Sn) and 727, 694 cm^{-1} (M = Pb). The NMR spectra tended to support the assigned structure (III). The NMR spectrum of (III, M = Sn) showed a multiplet at 7.18 to 7.90 ppm assignable to the protons of the three triphenyltin groups, and a sharp band at 8.23 ppm. The integration of this latter band suggested that it represents three protons, one of which (NH) was found to be exchangeable with D_2O. The sharp band at 8.30 ppm which remained after D_2O exchange may represent the ring protons at C-2, the effective environments surrounding these protons being virtually equivalent. The band which appeared at 8.05 ppm after D_2O exchange may represent one ring proton at C-8, adjacent to the NH group. The position of this band was found to be dependent upon the amount of D_2O added to the sample solution, each addition of D_2O causing an additional downfield shift. The other proton at C-8 may exist underneath the tin phenyl absorbance envelope and apparently its chemical shift does not depend on the concentration of D_2O present as does the one adjacent to the NH group.

It was found that (III, M = Sn) could also be prepared (60% yield) by allowing anhydrous 6-mercaptopurine to react with the complex formed between triphenyltin chloride and benzylamine. (III, M = Sn) was also obtained (77% yield) from the reaction of anhydrous 6-mercaptopurine with n-butyllithium and triphenyltin chloride.

The reaction of 6-mercaptopurine monohydrate with either tris(*p*-fluorophenyl)tin hydroxide, bis[tris(*p*-chlorophenyl)tin] oxide, or bis(tri-*p*-tolyltin) oxide gave, on the basis of the elemental analyses, *para*-substituted analogs of (III, M = Sn).

The reaction of 6-mercaptopurine monohydrate with bis(diphenylantimony) oxide gave 6-(diphenylantimony)mercaptopurine in 78% yield. The infrared spectrum showed a band at 2762 cm^{-1} characteristic[8] of hydrogen bonded NH. Bands attributable[5] to monosubstituted benzene were also present at 732 cm^{-1} and 695 cm^{-1}. Further indication that the bonding is between antimony and sulfur rather than between antimony and nitrogen is indicated by the fact that bis(diphenylantimony) oxide does not appear to react with purine.

EXPERIMENTAL

General comments

The purine intermediates were obtained from Mann Research Laboratories, Inc. New York, N.Y. and were not subjected to further purification. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Unless otherwise indicated, elemental analyses and Rast molecular weight determinations were performed by Dr. G. Weiler and Dr. F. B. Strauss, Microanalytical Laboratory, Oxford, England. Tin analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y. The infrared data were obtained using KBr pellets with a Perkin–Elmer Infracord. The far infrared data were obtained using KBr pellets with a Perkin–Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The ultraviolet data were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer using methanol (unless otherwise indicated) as solvent. The NMR spectra were determined at Sadtler Research Laboratories, Philadelphia, Pa. with a Varian A60A NMR spectrometer as a solution in deuterated dimethyl sulfoxide containing tetramethylsilane as an internal reference.

N-(Triphenylstannyl)purine

To a slurry of purine (1.20 g, 0.010 mole) and acetone (20 ml) was added a solution of bis(triphenyltin) oxide (3.58 g, 0.005 mole) in hot acetone (40 ml). The mixture was refluxed with stirring for 1 h and then was allowed to cool to 25°. Suction filtration afforded 3.86 g (82%) of product, m.p. 304–307° dec. (Found: C, 58.47; H, 4.06; N, 11.88; Sn, 24.71. $C_{23}H_{18}N_4Sn$ calcd.: C, 58.89; H, 3.87; N, 11.94; Sn, 25.30%.) IR: 730 and 698 cm^{-1} (monosubstituted benzene). Far IR: 664, 618, 604, 569, 494, and 456 cm^{-1}. UV: λ_{max} 209 mμ (ε 3.73×10^5) and 264 mμ (ε 8.9×10^4).

N-(Triphenylplumbyl)purine

To a stirred mixture of purine (1.20 g, 0.010 mole) and acetone (30 ml) was added a slurry of triphenyllead hydroxide (4.55 g, 0.010 mole) in acetone (100 ml). The resulting mixture was refluxed with stirring for 1 h and then was allowed to cool to 25°. Suction filtration afforded 4.46 g (80%) of product, m.p. 275–277° dec. (Found: C, 49.91; H, 3.60; N, 10.19. $C_{23}H_{18}N_4Ph$ calcd.: C, 49.54; H, 3.25; N, 10.05%.) IR: 726 and 694 cm^{-1} (monosubstituted benzene). Far IR: 648, 622, 572, 483, and 448 cm^{-1}. UV: λ_{max} 220 mμ (ε 4.33×10^4) and 264 mμ (ε 1.00×10^4).

N-(Triphenylstannyl)-6-chloropurine

To a stirred slurry of 6-chloropurine (containing 0.5% H_2O) (1.55 g, 0.010 mole) and acetone (20 ml) was added a solution of bis(triphenyltin) oxide (3.58 g, 0.005 mole) in hot acetone (40 ml). The mixture was refluxed with stirring for 1 h and then was allowed to cool to 25°. Petroleum ether (b.p. 30–60°) was then added to the cloud point. Cooling, followed by filtration, afforded 2.59 g of a yellow solid, m.p. 95–97° (193–198° dec.). A second crop of crystals (1.77 g), having the identical melting point (no depression on admixture), was also collected. Washing of the combined fractions with a 1/1 mixture of acetone/acetonitrile yielded 3.85 g (77%) of product, m.p. 100–101° (200° decomp.). (Found: N, 11.42. $C_{23}H_{17}ClN_4Sn$ calcd.: N, 11.17%.) IR: 733 and 699 cm^{-1} (monosubstituted benzene). Far IR: 655, 635, 550, 537, and 455 cm^{-1}. UV: λ_{max} 210 mμ (ε 3.74×10^5) and 265 mμ (ε 8.08×10^4).

N-(Triphenylplumbyl)-6-chloropurine

To a mixture of 6-chloropurine (containing 0.5% H_2O) (1.55 g, 0.010 mole) and acetone (30 ml) was added a slurry of triphenyllead hydroxide (4.55 g, 0.010 mole) in acetone (100 ml). The resulting mixture was refluxed with stirring for 1 h and then was allowed to cool to 25°. Addition of water to the cloud point resulted in the precipitation of a white solid, m.p. 217–219° dec. Recrystallization from methylene chloride/ethanol yielded 3.12 g (53%) of product, m.p. 230–232° dec. [Found: C, 46.67; H, 2.80; N, 9.65; mol. wt. (Rast), 550. $C_{23}H_{17}ClN_4Pb$ calcd.: C, 46.66; H, 2.89; N, 9.46%; mol. wt. 592.07.) IR: 726 and 693 cm^{-1} (monosubstituted benzene). Far IR: 658, 636, 615, 597, 556, 535, 504, and 450 cm^{-1}. UV: λ_{max} 222 mμ (ε 6.21 × 10^4) and 265 mμ (ε 2.01 × 10^4).

N-(Triphenylplumbyl)-6-methylmercaptopurine

To a mixture of 6-methylmercaptopurine (1.66 g, 0.010 mole) and acetone (30 ml) was added a slurry of triphenyllead hydroxide (4.55 g, 0.010 mole) in acetone (100 ml). The mixture was refluxed with stirring to afford a clear solution. The mixture was allowed to cool to 25°, and then water was added to the cloud point, resulting in the formation of a white precipitate. Filtration afforded 3.52 g of a white solid, m.p. 132–138°, which, on recrystallization from acetonitrile/water, gave 3.02 g (50%) of product, m.p. 131–132°. [Found: C, 47.86; H, 3.38; N, 9.55; mol. wt. (Rast), 554. $C_{24}H_{20}N_4SPb$ calcd.: C, 47.75; H, 3.34; N, 9.28%; mol. wt., 603.73.] IR: 728 and 694 cm^{-1} (monosubstituted benzene). Far IR: 657, 634, 550, 534, 503, 447, and 423 cm^{-1}. UV: λ_{max} 220 mμ (ε 6.04 × 10^4) and 284 mμ (ε 2.42 × 10^4).

Reaction of 6-methylmercaptopurine with bis(triphenyltin) oxide

To a stirred slurry of 6-methylmercaptopurine (1.330 g, 0.0080 mole) and acetone (20 ml) was added a solution of 1.432 g (0.0020 mole) of bis(triphenyltin) oxide in hot acetone (40 ml). The resulting mixture was refluxed with stirring for 1 h and then filtered with suction (while hot) to yield 1.560 g of a white solid, m.p. 228–229°.

The acetone filtrate was concentrated to yield an additional 0.894 g of product, m.p. 225–227°. The overall yield of product after processing of the residual filtrate was 2.562 g (94%). [Found: C, 53.19; H, 3.91; Sn, 17.95. $C_{30}H_{26}N_8S_2Sn$ (II) calcd.: C, 52.88; H, 3.85; Sn, 17.42%.] IR: 729 and 700 cm^{-1} (monosubstituted benzene). Far IR: 655, 629, 615, 596, 531, 506, 458, and 423 cm^{-1}. UV: λ_{max} 218 mμ (ε 5.29 × 10^4) and 288 mμ (ε 3.56 × 10^4).

In another run in which the molar ratio of 6-methylmercaptopurine/bis(triphenyltin) oxide was 2/1 the yield was 67% (30% of 6-methylmercaptopurine was recovered unchanged).

Reaction of 6-mercaptopurine monohydrate with bis(triphenyltin) oxide

To a slurry of 6-mercaptopurine monohydrate[9] (6.81 g, 0.040 mole) in acetone (200 ml) was added a solution of bis(triphenyltin) oxide (21.48 g, 0.03 mole) in acetone (300 ml). The addition was accompanied by the gradual formation of a white precipitate. The mixture was refluxed with stirring for 1 h, allowed to cool to 25°, and filtered to yield 21.47 g of (III, M = Sn), m.p. 214–215° dec. Recrystallization from ethanol raised the melting point to 216–217° decomp. [Found: C, 57.10; H, 3.97; N, 8.55; S, 4.67. $C_{64}H_{50}N_8S_2Sn_3$ (III, M = Sn) calcd.: C, 56.92; H, 3.66; N, 8.30; S, 4.75%.] IR: 730 and 698 cm^{-1} (monosubstituted benzene). Far IR: 665, 599, 544, 513, and 446 cm^{-1}. UV: λ_{max} 220 mμ (ε 13.5 × 10^5), 252 mμ (ε 9.1 × 10^3) 265 mμ (ε 8.1 × 10^3), 269 mμ (ε 6.0 × 10^3), and 330 mμ (ε 6.0 × 10^4).

A second and third crop, m.p. 214–215° dec. and 213–214° dec. respectively, were collected, raising the yield of (III, M = Sn) to 26.32 g (97%). No other products could be found.

Reaction of 6-mercaptopurine monohydrate with triphenyllead hydroxide

To a stirred mixture of 6-mercaptopurine monohydrate (3.40 g, 0.020 mole) and acetone (50 ml) was added a slurry of triphenyllead hydroxide (13.36 g, 0.030 mole) in acetone (225 ml). The mixture was refluxed with stirring for 1 h, allowed to cool to 25°, and then filtered to yield 6.99 g of (III, M = Pb), m.p. 197–198° dec. [Found: C, 47.39; H, 3.14; S, 3.43. $C_{64}H_{50}N_8S_2Pb_3$ (III, M = Pb) calcd.: C, 47.54; H, 3.12; S, 3.97%.] IR: 727 and 698 cm^{-1} (monosubstituted benzene). Far IR: 658, 637, 538, and 443 cm^{-1}. UV: λ_{max} 220 mμ (ε 1.86 × 10^6) and 300 mμ (ε 1.62 × 10^5).

A second and third crop, m.p. 196–197° dec. and 192–193° dec. respectively, were collected bringing the total yield to 14.81 g (92%). Repeated recrystallizations from ethanol did not raise the melting point.

Tris(p-fluorophenyl)tin hydroxide

To a stirred solution of tris(*p*-fluorophenyl)tin chloride[10] (20.0 g, 0.05 mole) in diethyl ether (200 ml) was added a solution of sodium hydroxide (2.0 g, 0.05 mole) in water (25 ml). The mixture was refluxed with stirring for 16 h and then allowed to cool to 25°. Suction filtration afforded 23.0 g of a white solid, m.p. 124–130°. Successive washing with hot methylene chloride, diethyl ether, and petroleum ether (b.p. 30–60°) afforded 7.3 g (35%) of product, m.p. 135–136°. (Found: C, 51.42; H, 3.22; Sn, 27.82. $C_{18}H_{13}OF_3Sn$ calcd.: C, 51.35; H, 3.11; Sn, 28.19%.) IR: 907 cm^{-1} (OH) and 813 cm^{-1} (1,4-disubstituted benzene). A band in the region of 774 cm^{-1} (SnOSn) was absent[11]. Far IR: 629, 578, 508, and 410 cm^{-1}. UV: λ_{max} in $CHCl_3$ 262 mμ (ε 1549) and 272 mμ (ε 1295).

Processing of the organic extracts increased the yield of hydroxide to 12.0 g (58%).

Bis[tris(p-chlorophenyl)tin] oxide

To a stirred solution of tris(*p*-chlorophenyl)tin chloride[12] (2.44 g, 0.005 mole) in diethyl ether (50 ml) was added 10 ml of a 10% aqueous solution of potassium hydroxide. The mixture was refluxed with stirring for 1 h, allowed to cool to 25°, and filtered to give 0.97 g of a white solid, m.p. 119–121°. Recrystallization from methylene chloride/petroleum ether (b.p. 30–60°) yielded 0.76 g (33%) of product, m.p. 121–123°. [Found: C, 47.20; H, 2.88; Sn, 25.05; mol. wt.[13] (dibromomethane, 37°), 1060. $C_{36}H_{24}Cl_6OSn_2$ calcd.: C, 46.86; H, 2.62; Sn, 25.73%; mol. wt., 922.73.] IR: 772 cm^{-1} (SnOSn) and 808 cm^{-1} (1,4-disubstituted benzene). A band in the region of 910 cm^{-1} (OH) was absent[11]. Far IR: 487 and 391 cm^{-1}. UV: λ_{max} in $CHCl_3$ 243 mμ (ε 1.80 × 10^4), 260 mμ (ε 4591), 266 mμ (ε 5144), and 272 mμ (ε 4614).

Processing of the mother liquors increased the yield of oxide to 1.41 g (61%).

Bis(tri-p-tolyltin) oxide

To a stirred solution of tri-*p*-tolyltin chloride[14] (8.6 g, 0.02 mole) in diethyl ether (150 ml) was added a solution of sodium hydroxide (0.8 g, 0.02 mole) in water (25 ml). The resulting clear solution was refluxed with stirring for 16 h and then allowed to cool to 25°. The organic layer was separated and dried over magnesium sulfate. Distillation of the solvent *in vacuo* followed by trituration of the residue with petroleum ether (b.p. 30–60°) yielded 5.0 g of a white solid, m.p. 103–104°. Recrystallization from petroleum ether (b.p. 30–60°) afforded 3.1 g (39%) of product, m.p.

106–107.5°. (Found: C, 62.58; H, 5.41. $C_{42}H_{42}OSn_2$ calcd.: C, 63.04; H, 5.29%.) IR: 764 cm^{-1} (SnOSn) and 799 cm^{-1} (1,4-disubstituted benzene). A band in the region of 910 cm^{-1} (OH) was absent[11]. Far IR: 635, 578, 479, and 402 cm^{-1}. UV: λ_{max} in $CHCl_3$ 258 mμ (ε 2157), 263 mμ (ε 2361), and 275 mμ (ε 1756).

Reaction of 6-mercaptopurine monohydrate with tris(p-fluorophenyl)tin hydroxide

To a stirred slurry of 6-mercaptopurine monohydrate (170 mg, 0.0010 mole) in acetone (5 ml) was added a solution of tris(*p*-fluorophenyl)tin hydroxide (632 mg, 0.0015 mole) in acetone (18 ml). The resulting clear solution was refluxed with stirring for 1 h and then was evaporated to dryness. The oily residue, on trituration with ethanol, afforded 419 mg of product, m.p. 226–227°. (Found: C, 51.19; H, 2.90; N, 7.75. $C_{64}H_{41}F_9N_8S_2Sn_3$ calcd.: C, 50.80; H, 2.73; N, 7.40%.) IR: 821 cm^{-1} (1,4-disubstituted benzene). Far IR: 625, 638, 596, 575, 544, 506, 439, and 413 cm^{-1}. UV: λ_{max} 218 mμ (ε 1.15 × 10^6), 262 mμ (ε 1.15 × 10^4), and 269 mμ (ε 9.16 × 10^3).

A second crop was isolated (270 mg, m.p. 216–218°) which upon recrystallization from acetonitrile raised the yield to 603 mg (80%).

Reaction of 6-mercaptopurine monohydrate with bis[tris(p-chlorophenyl)tin] oxide

To a stirred mixture of 6-mercaptopurine monohydrate (170 mg, 0.0010 mole) in acetone (5 ml) was added a slurry of bis[tris(*p*-chlorophenyl)tin] oxide (692 mg, 0.00075 mole) in acetone (18 ml). The mixture was refluxed with stirring for 1 h and then was cooled in an ice bath to yield, after filtration, 202 mg (29% recovery) of bis[tris(*p*-chlorophenyl)tin] oxide, m.p. 119.5–121.5°, no depression on admixture with an authentic sample.

The clear filtrate was evaporated to dryness, and the residue was stirred with ethanol. Suction filtration afforded 58 mg (34% recovery) of 6-mercaptopurine monohydrate, m.p. 310–313° dec., no depression on admixture with an authentic sample.

Concentration of the filtrate yielded 311 mg of a white solid, m.p. 174–200°. Two recrystallizations from acetonitrile afforded 112 mg (14%) of product, m.p. 210–211°. (Found: C, 46.43; H, 3.03; N, 6.94. $C_{64}H_{41}Cl_9N_8S_2Sn_3$ calcd.: C, 46.27; H, 2.49; N, 6.74%.) IR: 808 cm^{-1} (1,4-disubstituted benzene). Far IR: 639, 596, 547, 513, and 485 cm^{-1}. UV: λ_{max} 208 mμ (ε 9.15 × 10^4), 227 mμ (ε 1.41 × 10^5), 258 mμ (ε 7.14 × 10^3), 264 mμ (ε 7.40 × 10^3), 271 mμ (ε 7.14 × 10^3), and 330 mμ (ε 3.59 × 10^4).

Reaction of 6-mercaptopurine monohydrate with bis(tri-p-tolyltin) oxide

To a stirred slurry of 6-mercaptopurine monohydrate (170 mg, 0.0010 mole in acetone (5 ml) was added a solution of bis(tri-*p*-tolyltin) oxide (600 mg, 0.00075 mole) in acetone (18 ml). The mixture was refluxed with stirring for 1 h, allowed to cool to 25°, and filtered to give 203 mg (35%) of product, m.p. 203–204°. (Found: C, 59.36; H, 4.87; N, 7.88. $C_{73}H_{68}N_8S_2Sn_3$ calcd.: C, 59.34; H, 4.64; N, 7.58%.) IR: 797 cm^{-1} (1,4-disubstituted benzene). Far IR: 649, 635, 610, 593, 575, 542, 531, 502, 480, and 419 cm^{-1}. UV: λ_{max} 207 mμ (ε 8.31 × 10^4), 225 mμ (ε 9.61 × 10^4), 263 mμ (ε 5.76 × 10^3), 269 mμ (ε 5.32 × 10^3), and 330 mμ (ε 3.81 × 10^4).

The filtrate was evaporated to dryness, and the residue was recrystallized from acetonitrile to yield 255 mg of a white solid, m.p. 203–204°. The overall amount of product collected was therefore 596 mg (81%).

Reaction of 6-mercaptopurine monohydrate with bis(diphenylantimony) oxide

To a stirred slurry of 6-mercaptopurine monohydrate (1.70 g, 0.010 mole) in acetone (50 ml) was added a solution of bis(diphenylantimony) oxide (2.84 g, 0.005 mole) in acetone (75 ml). The mixture, after being refluxed with stirring for 1 h, was allowed to cool to 25° and then was filtered to give 3.42 g of product, m.p. 214–216°. (Found: C, 47.85; H, 3.09; N, 13.30. $C_{17}H_{13}N_4SSb$ calcd.: C, 47.80; H, 3.07; N, 13.12%.) IR: 2762 cm^{-1} (NH), and 731 and 695 cm^{-1} (monosubstituted benzene). Far IR: 599, 544, 529, 513, 457, 447, and 427 cm^{-1}. UV: λ_{max} 210 mμ (ε 3.58×10^4) and 330 mμ (ε 2.23×10^4).

A second crop of product (0.63 g, m.p. 214–215°) was collected; total yield, 4.06 g (95%).

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SUMMARY

The preparation of *N*-triphenylstannyl and *N*-triphenylplumbyl derivatives of purine, 6-chloropurine, and 6-methylmercaptopurine (triphenylplumbyl derivative only) is described. A novel complex was obtained from the reaction of 6-methylmercaptopurine with bis(triphenyltin) oxide. Novel complexes were also obtained from the reaction of 6-mercaptopurine monohydrate with bis(triphenyltin) oxide, triphenyllead hydroxide, tris(*p*-fluorophenyl)tin hydroxide, bis[tris(*p*-chlorophenyl)-tin] oxide, and bis(tri-*p*-tolyltin) oxide.

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