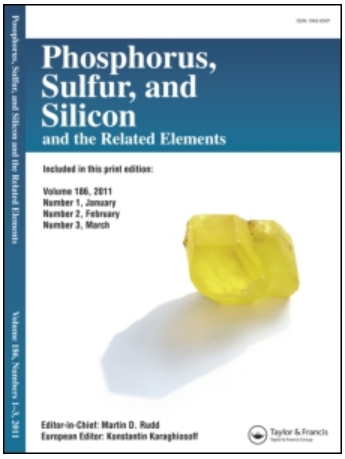

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DISPLACEMENT AND ELECTRON-TRANSFER REACTIONS OF SUBSTITUTED 2-CHLORO-1,3,2-BENZODIOXASTIBOLES WITH BASES

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DISPLACEMENT AND ELECTRON-TRANSFER REACTIONS OF SUBSTITUTED 2-CHLORO-1,3,2-BENZODIOXASTIBOLES WITH BASES

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2-Chloro-1,3,2-benzodioxastiboles undergo apparent nucleophilic displacement reactions on antimony in reactions with relatively weak bases. For example, 2-chloro-5-methyl-1,3,2-benzodioxastibole (**3**) gives 2-(*n*-butylamino)-5-methyl-1,3,2-benzodioxastibole (**14**) on treatment with *n*-butylamine. However, reaction of a 2-chloro-1,3,2-benzodioxastibole with a strong base leads, at least in part, to an apparent electron transfer reaction, with formation of a complex mixture of products. For example, treatment of 2-chloro-5-*tert*-butyl-1,3,2-benzodioxastibole (**2**) with phenylmagnesium bromide in tetrahydrofuran, with subsequent acid-catalyzed hydrolysis of the reaction mixture, gives rise to tert-butyl alcohol, catechol, 4-*tert*-butyl-catechol, phenol, triphenylantimony, biphenyl and methylphenylcarbinol.

Key Words: benzodioxastiboles; electron transfer; acid-catalyzed hydrolysis; organoantimony; nucleophilic displacement; mechanism.

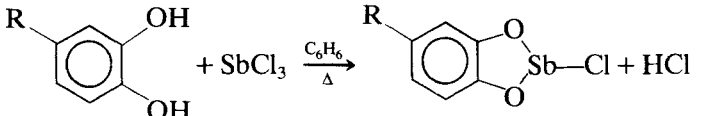
INTRODUCTION

We are in the process of preparing polymers containing organoantimony functional groups (which may be of use in petroleum refining, the preparation of bacteria-resistant coating materials, and the preparation of flame-retardant materials) based on poly(4-vinylcatechol)[1] as the fundamental starting material.[2] Therefore, in order to gain a better understanding of the reactions involved in the polymer grafting reactions, we have investigated a variety of reactions of 4-alkyl and other simple catechols with antimony reagents. These are the results which we are reporting in this paper.

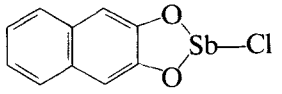
RESULTS AND DISCUSSION

Initial work was directed to the synthesis of readily available intermediates,[7–12] such as 2-chloro-1,3,2-benzodioxastibole (**1**), 2-chloro-5-*t*-butyl-1,3,2-benzodioxa-

stibole (**2**), 2-chloro-5-methyl-1,3,2-benzodioxastibole (**3**) and 2-chloro-naphtho[2,3-d]-1,3,2-dioxastibole (**4**).



1 R = H
2 R = *t*-Bu
3 R = Me



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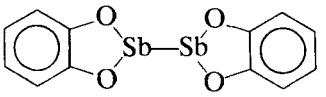
Anchisi, Cabiddu, Corda, Maccioni and Podda[13] have reported that products **5**, **6**, and **7** are obtained when 2-chloro-1,3,2-benzodioxastibole (**1**) is treated with triethylamine in the presence of phenol. Obviously, the structure of **7** is not possible, since there is no evidence that the antimony has been oxidized to the +5 state, and the tetravalent nitrogen is depicted without a positive charge and without the presence of an anion to balance the charge.



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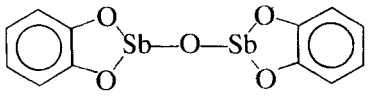

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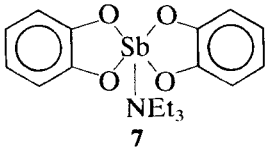

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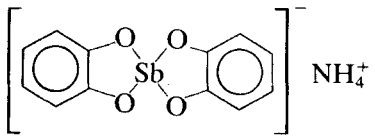
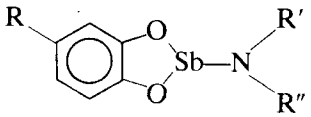
We have found that 2-chloro-1,3,2-benzodioxastibole (**1**) undergoes reaction with ammonia in tetrahydrofuran–methanol solution to give crystalline ammonium 2,2′-spirobis (1,3,2-benzodioxastibole)$^-$ (**8**) as a complex containing one equivalent of tetrahydrofuran, as shown by its NMR spectrum and microanalysis data. When heated *in vacuo* at 135°C for 24 hours, this complex gives ammonium 2,2′-spirobis(1,3,2-benzodioxastibole)$^-$ (**8**) free of tetrahydrofuran. The structure **8** is a reasonable one on the basis of the fact that metal salts of 2,2′-spirobis-(1,3,2-benzodioxastibole)$^-$ have been prepared and characterized.[14]



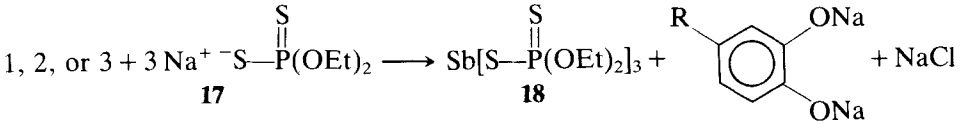
8

In view of the unusual results in the reaction of **1** with triethylamine reported by Anchisi *et al.*,[13] we decided to investigate reactions of compounds **2** and **3** with primary and secondary amines. The results are summarized in Table I. The major product in each of these cases is that which arises by an apparent nucleophilic displacement raction of the amine on antimony, with departure of chloride ion (and eventually the proton of the original amine). The products which are obtained are compounds **9–14**.[15]



Product	R	R′	R″
9	*t*-Bu	*i*-Pr	*i*-Pr
10	*t*-Bu	*n*-Pr	*n*-Pr
11	*t*-Bu	*t*-Bu	H
12	*t*-Bu	N-morpholino	
13	*t*-Bu	piperidino	
14	Me	*n*-Bu	H

In an apparently uncomplicated series of nucleophilic displacement reactions on antimony, compounds **1**, **2**, and **3**, respectively, undergo reaction with three equivalents of sodium 0,0-diethylphosphorodithioate (**17**) in ether solution to give antimony(III) *tris*-(0,0-diethylphosphorodithioate) (**18**)[16] in 59–60% yield plus the respective catechols.



Reactions of compounds **2–4** with relatively strong bases proved to be extraordinarily complex. Anchisi *et al.*[13] had reported that reaction of 2-chloro-1,3,2-benzodioxastibole (**1**) with sodium ethoxide in DMF or DMSO at 100°C gives 2,2′-*bis*-(1,3,2-benzodioxastibole) oxide (**6**) in 61% yield. However, we have found that reactions of **2**, **3**, and **4**, respectively, with sodium alkoxides, under a wide variety of conditions, give intractable mixtures of solids of high melting points. NMR spectral evidence indicates partial loss and/or migration of the substituent present in the 5-position in each of these reactions; i.e., the mixtures show the presence of at least three different magnetic environments for the original 5-R groups.

In order to gain some insight into the nature of these rearrangement or transfer processes, the reaction of 2-chloro-5-*t*-butyl-1,3,2-benzodioxastibole (**2**) with phenylmagnesium bromide in ether-THF was carried out, emphasis being placed on detection of hydrolysis products of the organoantimony compounds produced initially, rather than on isolation of the much more intractable organoantimony

TABLE I

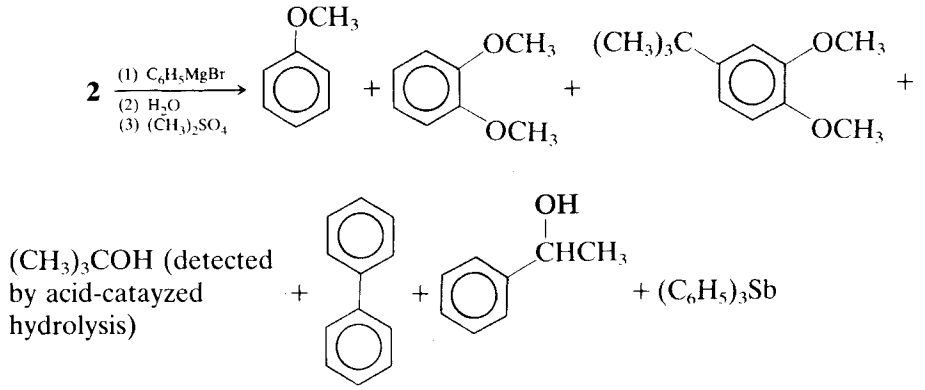
Reactions of equivalent amounts of 2-chloro-5-alkyl-1,3,2-benzodioxastiboles with amines in refluxing THF-EtOH (15 hr)[a]

Reagents	Product (% yield)	Mp °C	^{1}H NMR, δ (solvent)
2 + $(i\text{-Pr})_2NH$	**9** (72)	154–5	1.20 (s, 9H), 1.25 (s, 12H), 3.3 (m, 2H), 6.3–6.6 (m, 3H) (CCl_4)[b]
2 + $(n\text{-Pr})_2NH$	**10** (82)	166–8	0.9 (t, 6H), 1.2 (s, 9H), 1.6 (m, 4H), 2.8 (t, 4H), 6.4–6.7 (m, 3H) (DMSO-d_6)[c]
2 + t-$BuNH_2$	**11** (44)	149–50	1.3 (m, 18H), 1.9 (m, 1H), 6.6–6.8 (m, 3H) (DMSO-d_6)[d]
2 + morpholine	**12** (54)	230 (dec.)	1.2 (s, 9H), 3.2 (t, 4H), 3.8 (t, 4H), 6.4–6.6 (m, 3H) (DMSO-d_6)[e]
2 + piperidine	**13** (56)	200–2	1.2 (s, 9H), 1.6–2.0 (m, 6H), 2.9–3.2 (m, 4H), 6.3–6.6 (m, 3H) (DMSO-d_6)[f]
3 + n-$BuNH_2$	**14** (42, 87[g])	204–6 (dec.)	0.9 (m, 3H), 1.4 (m, 4H), 2.1(s, 3H), 2.8(m, 2H), 6.3 (m, 3H) (DMSO-d_6)[h]

[a] Elemental analyses were within ±0.4% of calcd. values.
[b] IR(KBr) 2950, 1480, 1420, 1260, 1120, 940, 800 cm^{-1}.
[c] IR(KBr) 2950, 1480, 1400, 1250, 1120, 920, 800, 640 cm^{-1}.
[d] IR(KBr) 3450, 2950, 1640, 1480, 1420, 1260, 1240, 1040, 920, 820, 640 cm^{-1}.
[e] IR(KBr) 2900, 1600, 1480, 1420, 1360, 1220, 1120, 1100, 1040, 940, 880, 860, 840, 800, 680, 640 cm^{-1}.
[f] IR(KBr) 2950, 2800, 2750, 2550, 2450, 1590, 1500, 1420, 1360, 1260, 1120, 1040, 940, 860, 840, 800, 700, 660, 560 cm^{-1}.
[g] In this case, yield improved by addition of one equivalent of 4-methylcatechol to reaction mixture.
[h] IR(KBr) 3350, 2950, 1600, 1580, 1480, 1305, 1230, 1210, 1110, 1005, 930, 830, 810 cm^{-1}.

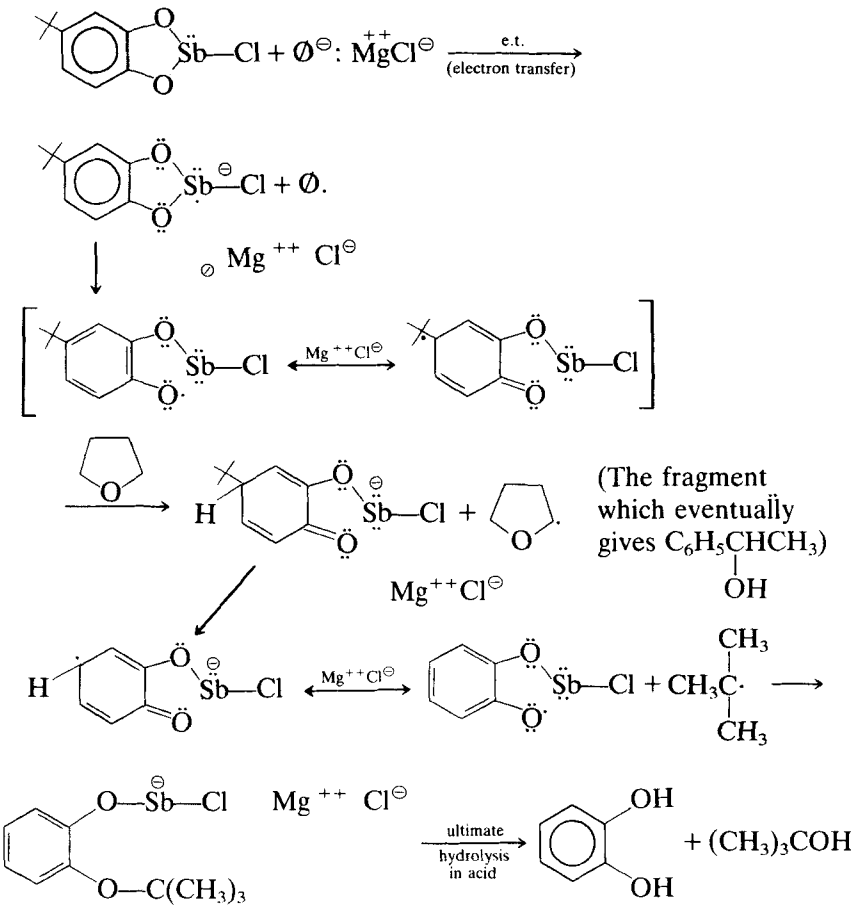
compounds themselves. The mixture obtained by reaction of phenylmagnesium bromide with **2**, with subsequent sulfuric acid-catalyzed hydrolysis of the products, was subjected to VPC analysis. *t*-Butyl alcohol, phenol and biphenyl were detected by VPC analysis (i.e., by spiking the mixtures with authentic samples, two different VPC columns being used). A control experiment proved that the *t*-butyl alcohol had not arisen by acid-catalyzed cleavage of **2**. Thus, although phenol and biphenyl could have arisen by side reactions of phenylmagnesium bromide, the *t*-butyl alcohol could have been formed only by fragmentation of a product or intermediate derived from **2**.

If *t*-butyl alcohol is present in the hydrolysate of the reaction mixture, it follows that another fragment of the original **2**, possibly catechol, must also be present. However, in the workup procedure, a compound such as catechol would have been lost in the aqueous wash step. Therefore, methylation of catechol with dimethyl sulfate was carried out on an alkaline hydrolysate of a reaction mixture of **2** with phenylmagnesium bromide.[17] The presence of 1,2-dimethoxybenzene and 4-*t*-butyl-1,2-dimethoxybenzene was determined by "mixture VPC" tests. Also, the mixture was subjected to GC/MS analysis, and anisole, biphenyl, triphenylantimony, and methylphenylcarbinol were also detected.

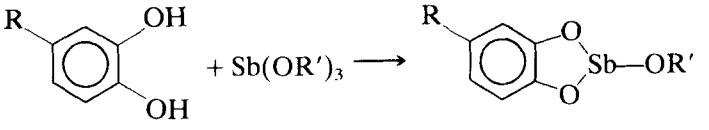


Although the ultimate product of substitution at antimony is triphenylantimony, a simple nucleophilic substitution pathway does not explain the formation of all of the products cited above. We believe that the initial step of at least one sequence of the reaction of phenylmagnesium bromide with **2** is an electron transfer reaction, and we propose the following detailed mechanism of reaction leading to the fragmentation products.[18]

As mentioned previously, we failed to obtain 2-alkoxy-1,3,2-benzodioxastiboles by reaction of the 2-chloro compounds with sodium alkoxides. Therefore, trimethyl antimonite (**19**) and triethyl antimonite (**20**) were prepared and caused to react with various catechols.[20–29] In this manner, 2-methoxy-1,3,2-benzodioxastibole (**21**), 2-methoxy-5-*t*-butyl-1,3,2-benzodioxastibole (**22**), 2-methoxy-5-methyl-1,3,2-benzodioxastibole (**23**), and 2-ethoxy-5-*t*-butyl-1,3,2-benzodioxastibole (**24**) were obtained in 90–92% yields. These compounds were found to undergo rapid hydrolysis to form insoluble Sb_2O_3 even in the air. In this regard, they resemble methoxytetraphenylantimony, dimethoxytriphenylantimony and



other related compounds in their ease of hydrolysis.[30–33] This also indicates that the alkoxy groups of these compounds possess considerable anionic character, particularly in contact with a polar, protic solvent.



19 R′ = Me
20 R′ = Et

21 R = H; R′ = Me
22 R = *t*-Bu; R′ = Me
23 R = Me; R′ = Me
24 R = *t*-Bu; R′ = Et

Although it is probably an oversimplification, the results discussed in this paper suggest that nucleophiles which have E_n[34] values less than about 2.5 undergo more or less normal nucleophilic displacement reactions on antimony in 2-chloro-1,3,2-benzodioxastiboles, while nucleophiles having greater E_n values undergo, at least partially, electron transfer reactions. Much additional work will be needed to verify and refine this generalization.

EXPERIMENTAL

Preparation of 2-*Chloro*-1,3,2-*benzodioxastibole* (**1**). This compound was prepared by the method of Funk and Kohler;[9,35] mp > 300° (dec.); H^1 NMR (DMSO-d_6) δ 6.6 (m). Anal. Calcd for $C_6H_4O_2SbCl$: C, 27.16; H, 1.52; Cl, 13.36. Found: C, 27.40; H, 1.42; Cl, 12.61.[36]

Preparation of 2-*Chloro*-5-*tert*-*butyl*-1,3,2-*benzodioxastibole* (**2**). A solution of 83.0 g (0.5 mole) of 4-*tert*-butylcatechol and 114 g (0.5 mole) of antimony trichloride in 350 mL of benzene was refluxed under an argon atmosphere. A precipitate formed during the period of reflux. After 4 days of reflux, the precipitate was collected by filtration, and 60.7 g (37.8% yield) of 2-chloro-5-*tert*-butyl-1,3,2-benzodioxastibole (**2**) was obtained; mp 298–300°C (dec.); H^1 NMR (DMSO-d_6) δ 6.6 (m, 3H), 1.2 (s, 9H). Anal. Calcd for $C_{10}H_{12}O_2SbCl$: C, 37.37; H, 3.76. Found: C, 37.48; H, 3.94.

Preparation of 2-*chloro*-5-*tert*-*butyl*-1,3,2-*benzodioxastibole tetrahydrofuran complex.* Exactly 3.21 g (0.01 mole) of 2-chloro-5-*tert*-butyl-1,3,2-benzodioxastibole was dissolved in 100 mL of tetrahydrofuran. After 2 days of reflux, a small amount of anhydrous hexane was added to the solution. A precipitate formed after the solution had been allowed to stand in a freezer (−10°C) overnight. The precipitate was dried under high vacuum for 5 hours; 3.0 g (76% yield) of 2-chloro-5-*tert*-butyl-1,3,2-benzodioxastibole tetrahydrofuran complex was obtained; mp >300°C (dec.); H^1 NMR (DMSO-d_6) δ 6.7 (m, 3H), 3.6 (m, 4H), 1.8 (m, 4H), 1.25 (s, 9H). Anal. Calcd for $C_{14}H_{20}O_3SbCl$: C, 42.72; H, 5.12; Cl, 9.01. Found: C, 41.19; H, 5.00; Cl, 8.83.

Preparation of 2-*chloro*-5-*methyl*-1,3,2-*benzodioxastibole* (**3**). A solution of 12.4 g (0.1 mole) of 4-methyl-catechol and 22.8 g (0.1 mole) of antimony trichloride in 250 mL of benzene was refluxed under an argon atmosphere, a precipitate forming during this period of reflux. After 2 days of reflux, the precipitate was collected by filtration, and 9.5 g (34% yield) of 2-chloro-5-methyl-1,3,2-benzodioxastibole (**3**) was obtained; mp 295–298°C (dec.); H^1 NMR (DMSO-d_6) δ 6.5 (m, 3H), 2.2 (s, 3H). Anal. Calcd for $C_7H_6O_2SbCl$; C, 30.10; H, 2.17; Cl, 12.69. Found: C, 30.03; H, 2.14; Cl, 12.57.

Preparation of 2-*Chloronaphtho*[2,3-*d*]-1,3,2-*dioxastibole* (**4**). To a suspension of 2,3-dihydroxynaphthalene (3.20 g, 0.02 mole) in toluene (140 mL), was added a solution of freshly sublimed antimony trichloride (4.56 g, 0.02 mole) in toluene (10 mL). The mixture was refluxed with stirring for 48 hr. A precipitate which had formed was collected, washed with warm methylene chloride and dried. There was obtained 4.43 g (63% yield) of **4**, mp 320°C (dec.); H^1NMR (DMSO-d_6) δ 7.70–8.05 (m, 2H), 7.35–7.60 (m, 4H). Anal. Calcd for $C_{10}H_6O_2SbCl$: C, 38.08; H, 1.92; Cl, 11.24. Found: C, 38.43; H, 1.99; Cl, 11.73.

Reaction of 2-*Chloro*-1,3,2-*benzodioxastibole* (**1**) *with Ammonia.* A solution of 4.00 g (0.015 mole) of 2-chloro-1,3,2-benzodioxastibole in 250 mL of anhydrous tetrahydrofuran and 30 mL of anhydrous methanol was heated to reflux under an argon atmosphere, a stream of dry ammonia gas being passed through the reaction mixture for 1.5 hr. The resulting cloudy mixture was filtered, and the filtrate was concentrated to half of its original volume; 1.7 g of white crystals were obtained after the filtrate had been allowed to stand at room temperature for 2 days. The white crystals were dried at room temperature under a high vacuum for 5 hours; mp >260°C (slow decomposition at 100°C, some gas being evolved); NMR (DMSO); δ 1.77 (m, 4H), 3.53 (m, 4H), 6.42 (m, 8H). Anal. Calcd for $C_{16}H_{20}NO_5Sb$; C, 44.80; H, 4.71; N, 3.27. Found C, 43.56; H, 5.08; N, 3.20. Presumably the crystalline material is ammonium 2,2′-spirobis(1,3,2-benzodioxastibole)$^-$ tetrahydrofuran complex on the basis of its NMR spectrum and analysis data. The white crystals were then dried by use of an Abderhalden drying pistol with *p*-xylene as the reflux liquid for 24 hours; 1.4 g (52.4%) of ammonium 2,2′-spirobis(1,3,2-benzodioxastibole)$^-$ (**8**) was obtained; mp 260°C (dec.); NMR (DMSO) δ 6.42 (m, 8H), 7.15 (s, 4H). A few drops of deuterium oxide was added to the sample in the NMR tube and the NMR spectrum taken again. The peak at $\delta = 7.15$ disappeared, and a new peak showed up at $\delta = 4.15$, which confirmed the existence of an ammonium group in the molecule. IR (nujol) λ max 3700, 3300, 2900, 1600, 1500, 1400, 1340, 1250, 1120, 1040, 940, 880, 800, 760 cm^{-1}. Anal. Calcd for $C_{12}H_{12}NO_4Sb$: C, 40.48; H, 3.39; N, 3.94. Found: C, 40.22; H, 3.24; N, 3.51.

Preparation of Compounds **9–14**. As a typical example, the preparation of 2-(*n*-butylamino)-5-methyl-1,3,2-benzodioxastibole (**14**) is described here. The salient features for the preparation of compounds **9–13** and the physical properties of all of the compounds **9–14**, are presented in Table I.

To a mixture of 2.79 g (0.01 mole) of 2-chloro-5-methyl-1,3,2-benzodioxastibole (**3**) and 1.24 g (0.01 mole) of 4-methylcatechol was added dropwise with stirring a solution of 1.46 g (0.02 mole) of *n*-butylamine in 15 mL of absolute ethanol. The mixture was refluxed for 15 hr., and, during this

period, a colorless precipitate formed. The solid was collected by filtration and washed with two 10 mL portions of tetrahydrofuran. The undissolved solid was crystallized from 1,4-dioxane to give 3.16 g (87% yield) of 2-(*n*-butylamino)-5-methyl-1,3,2-benzodioxastibole (**14**), mp 204–206°C (dec.).

Preparation of Compounds of Types **15** *and* **16**. The reaction of **2** with diethylamine will serve as a typical example. A solution of 3.22 g (0.01 mole) of 2-chloro-5-*t*-butyl-1,3,2-benzodioxastibole (**2**) in 150 mL of anhydrous tetrahydrofuran was refluxed under an argon atmosphere. By use of an addition funnel, a solution of 1.1 g (0.015 mole) of diethylamine in 15 mL of anhydrous ethanol was added dropwise. After completion of the addition, the reaction mixture was refluxed for another 8 hours. After having been cooled, a trace amount of precipitate which had formed was removed by filtration. The filtrate was concentrated to half of its original volume; 0.6 g (54.7%) of diethylamine hydrochloride was collected when the filtrate was cooled to −20°C; mp 227–230°C; NMR (DMSO) δ 1.43 (t, 3H), 3.50 (q, 2H). Anal. Calcd for $C_4H_{12}NCl$: C, 43.83; H, 11.04; N, 12.78; Cl, 32.34. Found: C, 43.72; H, 11.33; N, 12.66; Cl, 32.37.

The filtrate was evaporated to dryness, and a white precipitate was obtained. This white precipitate was washed with 50 mL of chloroform three times. There was obtained 1.5 g (57.2%) of diethylammonium 2,2′-spirobis(5-*t*-butyl-1,3,2-benzodioxastibole)$^-$ (**15** and/or **16**, R = *t*-Bu), mp 245–250°C (dec.); NMR (DMSO) δ 1.15 (s, 18H), 1.12 (t, 6H), 2.9 (q, 4H), 6.4 (m, 6H); IR (nujol) λ max 3000, 2620, 1600, 1560, 1520, 1460, 1430, 1360, 1330, 1280, 1140, 1120, 1100, 1080, 1000, 920, 900, 860, 760, 720, 680 cm^{-1}. Anal. Calcd for $C_{24}H_{36}NO_4Sb$: C, 54.39; H, 6.92; N, 2.67. Found: C, 54.19; H, 7.10; N, 2.62.

This and other compounds of type **15** are listed in Table II, together with appropriate conditions of reaction and physical constants. The spiro salts (analogs of **15**) were sometimes isolated, usually as minor products, from the filtrates of the reaction mixtures of compounds **9**–**14**.

Reaction of 2-*Chloro*-1,3,2-*Benzodioxastibole* (**1**) *with Sodium* 0,0-*diethyl phosphorodithioate* (**17**). A suspension of 2.65 g (0.01 mole) of 2-chloro-1,3,2-benzodioxastibole (**1**) and 6.24 g (0.03 mole) of sodium 0,0-diethyl phosphorodithioate (**17**) in 300 mL of anhydrous ether was refluxed for 3 days under an argon atmosphere. The resulting mixture consisted of a light-yellow solution and an undissolved solid, which was collected by filtration. The filtrate was then evaporated to dryness; 3.49 g (54% yield) of antimony *tris*-(0,0-diethyl phosphorodithioate) (**18**) was collected; mp 56°C; NMR ($CDCl_3$) δ 1.38 (t, 3H, J = 7 Hz), 4.18, 4.32 (overlapping quartets, 2H), in agreement with reported[16] values.

Reactions of **2** and **3** with **17** gave similar results.

Reaction of 2-*Chloro*-5-*t*-*butyl*-1,3,2-*Benzodioxastibole* (**2**) *with Phenylmagnesium Bromide.* Phenylmagnesium bromide (6.7 mL, 0.02 mole) in ether was added in a drop-wise manner to a solution of 6.42 g (0.02 mole) of 2-chloro-5-*t*-butyl-1,3,2-benzodioxastibole (**2**) in 100 mL of anhydrous tetrahydrofuran under an argon atmosphere. The reaction mixture was stirred at −70°C for 2.5 hours. After having been warmed to room temperature, tetrahydrofuran was partially removed by evaporation until about 10 mL of solution remained. Ten mL of 6 *M* sulfuric acid was added to this solution, and then the resulting solution was heated at 60°C for one hour. A steam distillation was set up to distill any volatile organic compound present in the reaction mixture. About 50 mL of distillate was collected, which was then extracted with three 50 mL portions of ether. The ether layer was dried over anhydrous magnesium sulfate and analyzed by gas chromatography. The presence of *t*-butyl alcohol, phenol and biphenyl was confirmed by co-injection with authentic samples, with two different columns being used; gas chromatographic analysis conditions, detector temperature 265°C; carrier gas helium; flow rate 24 mL/min. For identification of *t*-butyl alcohol: column (a) 3% OV-17 (phenyl), 6′ × 1/8″; temperature 55°C (isothermal); retention time 2.2 minutes; column (b) SE-30 (methyl), 6′ × 1/8″; temperature 60°C (isothermal); retention time 0.8 minutes. For identification of phenol: column (a) 3% XE-60; 12′ × 1/8″; temperature 120°C (isothermal); retention time 2.6 minutes. Column (b) SE-30 (methyl; 6′ × 1/8″; temperature 120°C (isothermal); retention time 0.8 minutes. For identification of biphenyl: column (a) 3% XE-60; 12′ × 1/8″; temperature 120°C (isothermal); retention time 5.5 minutes. Column (b) SE-30 (methyl), 6′ × 1/8″; temperature 120°C (isothermal); retention time 4.7 minutes.

Preparation of 4-*t*-*butyl*-1,2-*dimethoxybenzene.* Dimethyl sulfate (7.5 g, 0.059 mole) and 15.1 g (0.09 mole) of 4-*t*-butylcatechol were dissolved in 30 mL of methyl alcohol. After having been cooled to −5°C, a solution of sodium hydroxide (15 g, 0.0267 mole in 35 mL of water) was added to the alcohol solution all at once. A vigorous reaction took place; the methylation reaction was complete in three minutes. After dilution with 100 mL of water, the aqueous solution was extracted with two 100 mL portions of ether. The ether layer was washed with water until it was neutral to litmus paper,

TABLE II

Preparation of spiro salts of types **15**, **16** and **25** in refluxing THF-EtOH (8 hr) (See Note 15)[a]

Stibole	Amine (equivs.)	Added Reagent (equivs.)	Product Cation	Product Anion	Mp °C	Yield (%)
2	Et_2NH (1.0)	None	$Et_2NH_2^+$	15/16 (R = *t*-Bu)	250 (dec.)	25[b]
2	Et_2NH (1.5)	None	$Et_2NH_2^+$	15/16 (R = *t*-Bu)	250 (dec.)	57
2	Et_2NH (2.0)	4-*t*-butylcatechol (1.0)	$Et_2NH_2^+$	15/16 (R = *t*-Bu)	250 (dec.)	68
1	Et_2NH (1.0)	None	$Et_2NH_2^+$	15 (R = H)	257–60 (dec.)	40[c]
1	Et_2NH (2.0)	Catechol (1.0)	$Et_2NH_2^+$	15 (R = H)	257–60 (dec.)	60
2	*i*-Pr_2NH (1.0)	None	*i*-$Pr_2NH_2^+$	15/16 (R = *t*-Bu)	100–3	72[d]
2	*i*-Pr_2NH (2.0)	4-*t*-butylcatechol (1.0)	*i*-$Pr_2NH_2^+$	15/16 (R = *t*-Bu)	100–3	84
2	*t*-$BuNH_2$ (2.0)	4-*t*-butylcatechol (1.0)	*t*-$BuNH_3^+$	15/16 (R = *t*-Bu)	119–20	61[e]
2	Morpholine (2.0)	4-*t*-butylcatechol (1.0)	$C_4H_{10}ON^+$	15/16 (R = *t*-Bu)	172–3	78[f]
3	Et_2NH (1.0)	None	$Et_2NH_2^+$	15/16 (R = Me)	287–9 (dec.)	30[g]
3	Et_2NH (2.0)	4-methylcatechol (1.0)	$Et_2NH_2^+$	15/16 (R = Me)	287–9 (dec.)	60
4	Et_2NH (2.0)	2,3-dihydroxynaphthalene (1.0)	$Et_2NH_2^+$	25[h]	252–4 (dec.)	43[i]

[a] Elemental analyses were within ±0.4% of calcd. values.

[b] Spectral data given in experimental section.

[c] ^1H NMR (DMSO-d_6): δ 1.1 (t, 6H), 2.95 (q, 4H), 4.0 (s, 2H), 6.3 (m, 8H); IR(KBr) 2950, 2700, 1480, 1260, 820, 760, 640 cm^{-1}.

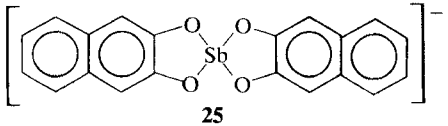
[d] ^1H NMR(CCl_4): δ 1.2 (s, 18H), 1.4 (m, 12H), 3.6 (m, 2H), 6.4–6.8 (m, 6H); IR(KBr) 2900, 2500, 1600, 1420, 1350, 1260, 1240, 1120, 940, 800, 650 cm^{-1}.

[e] ^1H NMR (DMSO-d_6): δ 1.1 (s, 18H), 1.4 (s, 9H), 6.4–6.8 (m, 6H); IR(KBr) 2950, 1600, 1490, 1420, 1380, 1360, 1260, 1240, 1120, 1040, 930, 860, 800, 640 cm^{-1}.

[f] ^1H NMR (DMSO-d_6): δ 1.3 (s, 18H), 3.2 (t, 4H), 3.8 (t, 4H), 6.4–6.8 (m, 6H); IR(KBr) 2950, 2820, 2420, 1600, 1480, 1400, 1360, 1260, 1180, 1120, 1100, 1020, 940, 880, 850, 820, 590, 560, 500 cm^{-1}.

[g] ^1H NMR ($CDCl_3$): δ 1.2 (t, 6H), 2.2 (s, 6H), 3.2 (q, 4H), 4.7 (s, 2H), 6.5 (m, 6H); IR(KBr) 3300, 2950, 2590, 1490, 1260, 1130, 960, 820 cm^{-1}.

[h]



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[i] ^1H NMR (DMSO-d_6): δ 1.2(t, 6H), 2.9(q, 4H), 4.0 (s, 2H), 6.9 (m, 8H), 7.3 (m, 4H); IR(KBr) 2950, 2650, 2500, 1460, 1250, 1180, 870, 770 cm^{-1}.

dried over calcium chloride and then concentrated to dryness to give an oil. This was induced to crystallize from pentane to give 2.17 g (20% yield) of 4-*t*-butyl-1,2,-dimethoxybenzene, mp 32–33°C; NMR ($CDCl_3$); δ 6.69–7.1 (m, 3H), 4.0 (s, 3H), 3.95 (s, 3H); 1.4 (s, 9H), in substantial agreement with literature values.[37]

Reaction of 2-Chloro-5-t-butyl-1,3,2-benzodioxastibole (**2**) *with Phenyl-magnesium Bromide and Subsequent Methylation.* The reaction was carried out as described previously up to the point at which the tetrahydrofuran solution was allowed to warm to room temperature. Then, tetrahydrofuran was partially removed by evaporation until about 30 mL of solution remained. Ten mL of 6 *M* sulfuric acid was added to this solution, and the resulting solution was heated to 60°C for one hour. After having been cooled to room temperature, some inorganic salt which had formed was removed by filtration. The filtrate was made basic with concentrated sodium hydroxide solution. Dimethyl sulfate (2.53 g, 0.02 mole) was added to this basic solution at 5°C, then the solution was heated to 70°C for 15 minutes. The aqueous solution was extracted with three 50 mL portions of ether. The ether layer was then washed with water until it was neutral to litmus paper, dried over sodium sulfate and analyzed by gas chromatography. The presence of 1,2-dimethoxybenzene and 4-*t*-butyl-1,2-dimethoxybenzene was confirmed by coinjection with authentic samples, with two different columns. Gas chromatographic analysis conditions: detector temperature 270°C; injector temperature 180°C; carrier gas helium; flow rate 24 mL/min. For identification of 1,2-dimethoxybenzene: column (a) 3% OV-17 (phenyl); 6′ × 1/8″; temperature initially 80°C, program 6°C/min; retention time 8.1 minutes. Column (b) SE-30 (methyl); 6′ × 1/8″; temperature initially 80°C; program 6°C/min; retention time 8.8 minutes. For identification of 4-*t*-butyl-1,2-dimethoxybenzene: column (a) SE-30 (methyl); 6′ × 1/8″; temperature 130°C (isothermal); retention time 10.6 minutes. Column (b) 3% OV-17 (phenyl), 6′ × 1/8″; temperature 130°C (isothermal); retention time 7.2 minutes. GC/MS spectra were also taken; gas chromatography conditions; DP5-15 meter capillary column; initial temperature 40°C, program 6°C/min; final temperature 250°C. Spectra[38] #4 and #5, anisole, MS 108 [(M^+), base peak], 93 [(M—CH_3)$^+$], 78 ((M—OCH_2)$^+$]. Spectra #35 and #37, octamethylcyclotetrasiloxane (silicone grease), MS; m/e 281 [(M)$^+$ base peak]. Spectra #64 and #75, α-methylbenzenemethanol, MS; m/e 122 (M^+), 107 [(M—CH_3)$^+$], 105 [(M—OH)$^+$], 78 [(M—CH_2COH—H)$^+$ base peak], 77 [(M—CH_3CHOH)$^+$]. Spectrum #93, 1,2-dimethoxybenzene, MS; m/e 138 [(M^+), base peak], 123 [(M—CH_3)$^+$], 95 [(M—CH_3)$^+$]. Spectrum #97, silicone grease impurities, MS; m/e 355 (M^+). Spectrum #172, biphenyl, MS; m/e 154 [(M^+), base peak], 153 [(M—H)$^+$], 76 [(M − C_6H_5—H)$^+$]. Spectrum #194, 4-*t*-butyl-1,2-dimethoxybenzene, m/e 194 (M^+), 179 [(M—CH_3)$^+$, base peak], 164 [(M—CH_2O)$^+$]. Spectra #441 and #532, triphenylstibine, m/e 352 (M^+), 275 [(M—C_6H_5)$^+$], 198 [(M—C_6H_5—C_6H_5)$^+$, base peak].

Preparation of 2-Methoxy-5-tert-butyl-1,3,2-benzodioxastibole (**22**). A solution of 1.73 g (0.0104 mole) of 4- *tert*-butylcatechol in 50 mL of anhydrous methanol was added in a drop-wise manner to a solution of 2.24 g (0.0104 mole) of trimethyl antimonite (**19**)[20] in 150 mL of anhydrous methanol under an argon atmosphere. A white precipitate formed immediately. After one hour of stirring at room temperature, the precipitate was collected by filtration under an argon atmosphere; 2.96 g (90% yield) of 2-methoxy-5-*tert*-butyl-1,3,2-benzodioxastibole (**22**) was obtained; mp >300°C;

TABLE III

Properties of 2-Alkoxy-1,3,2-benzodioxastiboles[a]

Compound	Mp °C	Yield (%)	^{1}H NMR (DMSO-d_6) δ
21	300–10 (dec.)[b]	90	3.4 (s, 3H), 6.6 (m, 4H)[c,d]
22	>300 (dec.)	90	Data given in experimental section
23	278–86	92	2.2 (s, 3H), 3.4 (s, 3H), 6.5 (m, 3H)
24	237–8	92	1.0 (t, 3H), 1.2 (s, 9H), 3.6 (q, 2H), 6.8 (m, 3H)

[a] Analyses were within ±0.3% of calcd. values.
[b] Lit.[22] mp 101°C (dec.).
[c] Lit.[22] ^{1}H NMR (DMSO-d_6) δ 4.05(s), 7.25(m).
[d] *Anal.* Calcd for $C_7H_7O_3Sb$: C, 32.23; H, 2.70. Found: C, 32,20; H, 6.24. Wieber, Baumann and Burschka[22] did not provide an elemental analysis of their compound. However, they did provide a crystal and molecular structure of material freshly crystallized from methanol. They stated that "Interaction with oxygen atoms of two neighboring molecules enlarges the coordination number on the antimony to five, thus forming a structure with infinite chains along the α-axis.

NMR (DMSO-d_6) δ 6.6 (m, 3H), 3.4 (s, 3H), 1.29 (s, 9H); IR (nujol) 2900, 1600, 1520, 1480, 1400, 1280, 1200, 1140, 1020, 810 cm^{-1}. Anal. Calcd for $C_{11}H_{15}O_3Sb$; C, 41.67; H, 4.77. Found: C, 41.48; H, 4.86.

The yields and physical properties of the esters **21–24** are presented in Table III. The preparation of triethyl antimonite (**20**) was also based on the procedure of Meerwein and Bersin.[20]

ACKNOWLEDGMENT

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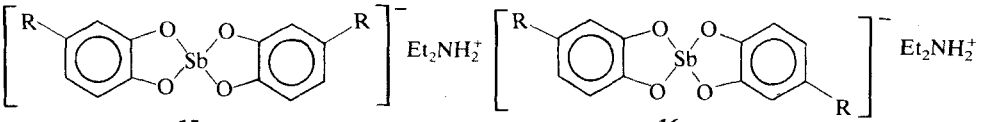
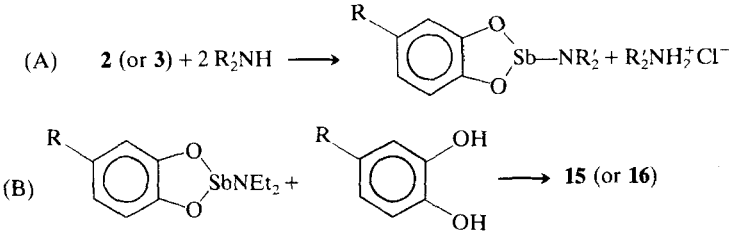


15 **16**

Although we do not have a complete understanding of the mechanisms of these reactions, examination of the balanced equations for the following reactions indicate an explanation for the experimental facts that (1) yields of 2-alkylamino-1,3,2-dioxastiboles, **9–14**, are increased by the presence of two equivalents of amine per one equivalent of **2** or **3**; and (2) yields of spiro salts are increased by the presence of one equivalent of the parent catechol and two equivalents of amine per one equivalent of **2** or **3**.



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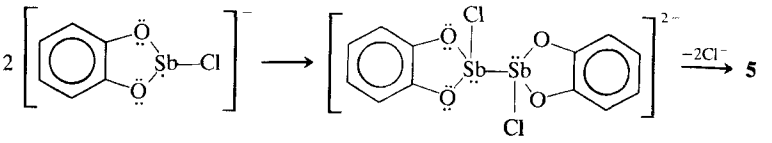
18. On the assumption that an initial electron transfer reaction can occur between **1** and triethylamine, the formation of **5** from these reagents can be explained by a related mechanism.



Also, compound **7**[13] is probably the triethylammonium salt of the anion of **8**.
19. Anchisi *et al.*[13] have also reported that **5** can be obtained from **1** by the action of sodium metal, pyridine or *n*-butyllithium. These reactions, particularly that with sodium metal, lend credence to the mechanism proposed above.[18]
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