Preparation and Reactions of Di-*n*-butylantimonylithium and Di-*n*-butylantimonymagnesium Reagents[1]

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The preparation of diphenylantimonysodium[2] from diphenyliodostibine and sodium in liquid ammonia as well as diphenylantimonylithium[3] by lithium cleavage of triphenylstibine previously has been described. The preparation of the corresponding dialkylantimony organometallics have not been described.[4] This note describes the preparation and some of the reactions of di-*n*-butylantimonylithium and di-*n*-butylantimonymagnesium in tetrahydrofuran (THF).

These reagents can be prepared conveniently in good yield by the reaction of di-*n*-butylbromostibine with either freshly cut lithium strips or magnesium shavings in tetrahydrofuran at room temperature (eq. 1 and 2).

$$(n\text{-}C_4H_9)_2SbBr + 2\ Li \xrightarrow{\text{THF, } 28°} (n\text{-}C_4H_9)_2SbLi + LiBr \quad (1)$$

$$2(n\text{-}C_4H_9)_2SbBr + 2Mg \xrightarrow{\text{THF, } 28°} [(n\text{-}C_4H_9)_2Sb]_2Mg + MgBr_2 \quad (2)$$

Substitution of either ethyl ether or dioxane for tetrahydrofuran completely inhibits the formation of di-*n*-butylantimonymagnesium even in the presense of ethyl bromide. Di-*n*-butylantimonylithium (unlike diphenylantimonylithium) could not be prepared by cleavage of tri-*n*-butylstibine by lithium in refluxing tetrahydrofuran.

Di-*n*-butylallylstibine was obtained when allyl bromide reacted with either di-*n*-butylantimonylithium (73%) or di-*n*-butylantimonymagnesium (31%). Reaction of chlorotrimethylsilane with di-*n*-butylantimonymagnesium yielded trimethylsilyldi-*n*-butylstibine (22%), a colorless, highly pyrophoric liquid. Instead of the desired tetra-*n*-butyldistibine, reaction of di-*n*-butylbromostibine with the magnesium reagent yielded tri-*n*-butylstibine (37%) along with antimony metal and a black, air-reactive solid believed to be polymeric *n*-butylstibine.[5]

Considerable tri-*n*-butylstibine was isolated from both the methanolysis (43%) and carbonation (66%) of the di-*n*-butylantimonymagnesium reagent at −60°. An examination of the infrared spectra of both reaction mixtures just after reaction indicated the absence of either the desired hydride or carboxylate. This is consistent with the formation, initially, of the distibine in the methanolysis or carbonation of the di-*n*-butylantimonymagnesium reagent followed by its thermal and catalytic decomposition to tri-*n*-butylstibine, antimony, and polymeric *n*-butystibine upon work-up.

Experimental[6]

Di-*n*-butylbromostibine.—The procedure used is a modification of Morgan and Davies.[7] A flask containing 221 g. of tri-*n*-butylantimony dibromide (0.488 mole) was heated slowly with stirring to a bath temperature of 220° over a period of 4 hr. At a bath temperature of 210°, *n*-butyl bromide began to distil out of the reaction mixture and continued until 50 ml. (93%) was obtained. The reaction mixture was fractionally distilled two times to yield 113.0 g. (74%) of di-*n*-butylbromostibine, b.p. 68° (0.10 mm.). The product was a mobile yellow liquid which did not fume in the air but slowly deposited di-*n*-butylantimony oxybromide when left in an open beaker.

Anal. Calcd. for $C_8H_{18}BrSb$: Br, 25.3. Found: Br, 25.1.

Diisobutylbromostibine, b.p. 64–66° (0.10 mm.), was similarly prepared in 81% yield by the pyrolysis of triisobutylantimony dibromide.

Di-*n*-butylallylstibine.—To a stirring mixture of 1.32 g. of freshly cut lithium strips (0.19 g.-atom) in 50 ml. of THF at room temperature, 30.0 g. of di-*n*-butylbromostibine (0.095 mole) in 50 ml. of THF was added dropwise over a period of 1 hr. The temperature rose to 45° and remained there throughout the addition while the reaction mixture gradually turned a deep red color. After an additional 2 hr. of stirring at room temperature, the reaction mixture was filtered. No unchanged lithium was observed (100% conversion). A 50-ml. THF solution containing 11.5 g. of allyl bromide (0.095 mole) then was added to the reaction mixture (15 min.) and stirring was maintained overnight. The reaction mixture (now yellow) was hydrolyzed with 20 ml. of saturated ammonium chloride solution at 0° and the THF layer was dried over magnesium sulfate. Fractional distillation of the THF layer yielded 19.0 g. (73%) of di-*n*-butylallylstibine, b.p. 54–56° (0.05 mm.).

Anal. Calcd. for $C_{11}H_{23}Sb$: Sb, 43.9. Found: Sb, 44.1.

The infrared spectrum of the product showed bands characteristic of the allyl group ($\nu_{C=C}$ 1625 cm.$^{-1}$) and butyl groups (2880, 1455, 1140, and 865 cm.$^{-1}$.).

Di-*n*-butylallylstibine was similarly prepared in 31% yield by the reaction of di-*n*-butylantimonymagnesium with allyl bromide and by the reaction of allylmagnesium bromide with di-*n*-butylbromostibine (54%). All infrared spectra were superimposable.

Trimethylsilyldi-*n*-butylstibine.—Di-*n*-butylantimonymagnesium was prepared by the dropwise addition (2 hr.) of 30.0 g. of di-*n*-butylbromostibine (0.095 mole) in 50 ml. of THF to a stirring mixture of 2.3 g. of magnesium shavings (0.10 g.-atom) in THF. Filtration of the dark brown reaction mixture yielded 0.15 g. of unchanged magnesium (94% conversion) as well as magnesium bromide. To the filtered reaction mixture was added a 25-ml. THF solution of 10.8 g. of chlorotrimethylsilane (0.10 mole) over a period of 15 min., after which stirring was maintained overnight at room temperature. After filtration, the mixture was fractionally distilled and the fraction distilling at b.p. 80–87° (0.40 mm.) was retained and redistilled to yield 6.5 g. (22%) of trimethylsilyldi-*n*-butylstibine, b.p. 48–50° 0.025 mm.). The product was a colorless water-reactive liquid which spontaneously ignited upon contact with the atmosphere.

Anal. Calcd. for $C_{11}H_{27}SbSi$: Si, 9.1. Found: Si, 8.7.

The infrared spectrum of the product showed bands characteristic of the trimethylsilyl group (1240, 830, and 810 cm.$^{-1}$) as well as bands characteristic of butyl groups.

Attempted Preparation of Tetra-*n*-butyldistibine.—Di-*n*-butylbromostibine (20.0 g., 0.063 mole) in 20 ml. of THF was added to to di-*n*-butylantimonymagnesium reagent prepared from 20 g. of di-*n*-butylbromostibine (0.063 mole) and 1.45 g. of magnesium (0.063 g.-atom), and the reaction mixture was allowed to stir overnight at room temperature. Filtration and fractional distillation of the THF solution yielded 7.0 g. (37%) of tri-*n*-butylstibine, b.p. 62–64° (0.05 mm.), lit. b.p. 131° (12 mm.).

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(1) The structures of these reagents have not been elucidated. For the sake of conciseness the above nomenclature is used throughout the discussion.

(2) L. A. Woods and H. Gilman, *Proc. Iowa Acad. Sci.*, **48**, 251 (1941).

(3) D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958).

(4) The preparation of tetramethyldistibine from dimethylbromostibine and sodium or lithium in liquid ammonia has been described [see A. E. Burg and L. R. Grant, *J. Am. Chem. Soc.*, **81**, 1 (1959)].

(5) The thermal decomposition of tetramethylstibine yielded trimethylstibine and antimony while a silicone grease-catalyzed decomposition of the distibine yielded trimethylstibine and polymeric methylstibine (see ref. 4, p. 5).

(6) Tetrahydrofuran, ethyl ether, and dioxane were distilled over sodium ribbon and stored under nitrogen. A nitrogen atmosphere was used for all reactions and other manipulations. The toxicities of the alkyl stibines are unknown, and it is advisable to use caution in the handling of these materials.

(7) G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.* (London), **110**, 523 (1926).

Anal. Calcd. for $C_{12}H_{27}Sb$: Sb, 41.6. Found: Sb, 41.4.

Attempted preparation of the distibine using di-*n*-butylantimonylithium also resulted in 22% tri-*n*-butylstibine. In both reactions an antimony mirror was noted in the distilling flask. The distillation residue was a black solid which contained butyl groups (infrared) and which also gave a qualitative test for antimony. Upon standing in the air, this black solid turned white. The similarities in physical properties between polymeric methylstibine (see ref. 4, p. 5) and this material strongly suggest that it is polymeric *n*-butylstibine.

An Abnormal Fluorination with Sulfur Tetrafluoride

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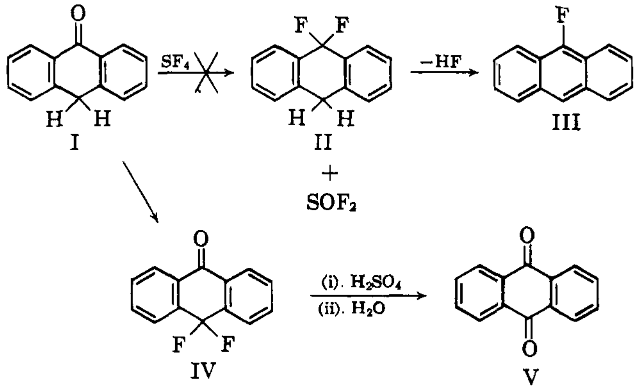
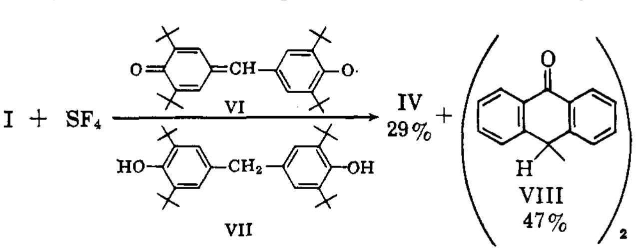
The recent discovery and exploitation of the general reaction of sulfur tetrafluoride with the carbonyl function to produce *gem*-difluorides[1] suggested a feasible synthesis of 9-fluoroanthracene, which was required for another investigation. Sulfur tetrafluoride would be expected to convert anthrone (I) to 9,9-difluoro-9,10-dihydroanthracene (II), which should easily lose the elements of hydrofluoric acid under conditions of either acid or base catalysis to give 9-fluoroanthracene (III). The product of the reaction was, however, neither II nor III, but 10,10-difluoroanthrone (IV). Compound IV was identified by its carbon–hydrogen analysis, by the presence in the infrared spectrum of an absorption at 1677 cm.$^{-1}$ characteristic of aromatic ketones,[2] and by the absence of n.m.r. signals characteristic of diarylmethylene protons.[3] The position of the fluorine substituents was confirmed by the hydrolysis of IV to anthraquinone (V) under acid conditions, a reaction typical of *gem*-difluorides which can form conjugated ketones by hydrolysis.[4] The best yield (85%) of IV was obtained when methylene chloride was employed as a solvent. In the absence of solvent, the yield of IV was 48%.



Although sulfur tetrafluoride is an oxidizing agent under some circumstances,[5] it has not been observed before to attack the carbon–hydrogen bond under mild conditions. Such attack suggests a free-radical chain mechanism analogous to halogenations by molecular chlorine and bromine. To test this hypothesis, the fluorination was run in the presence of small amounts of the radical scavenger, 2,6-di-*t*-butyl-*α*-(3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy radical (VI)[6] and the antioxidant, 4,4′-dihydroxy-3,5,3′,5′-tetra-*t*-butyldiphenylmethane (VII). It was expected that methylenic fluorination would be inhibited and recovery of starting material would be possible. If this had been the case, the reaction with sulfur tetrafluoride would have been repeated in the presence of VI and VII at increased temperatures in the hope that the normal carbonyl fluorination would occur. The result, however, of the addition of VI and VII to the reaction mixture was to cause the formation of 10,10′-bianthrone (VIII) in 47% yield. The yield of IV was reduced to 29%. Compound I was recovered quantitatively from a control experiment in which an ethylene chloride solution of I, containing small amounts of VI and VII, was heated at the temperatures used in the inhibited fluorination of I.



The fact that VI and VII inhibit to some extent the formation of IV supports the proposed radical chain mechanism. To account for the formation of VIII, an ionic Friedel–Crafts reaction of fluoroanthrone with the phenolic tautomer of anthrone may be suggested, but the matter has been investigated no further in this work.

Experimental[7]

10,10-Difluoroanthrone (IV).—Anthrone, 19.4 g. (0.100 mole), was purged with nitrogen under vacuum in a 183-ml. stainless steel reaction bomb, 24.5 g. (0.226 mole) of sulfur tetrafluoride (E. I. du Pont de Nemours and Co., Organic Chemicals Dept., technical) and 5.5 g. (0.28 mole) of anhydrous hydrofluoric acid were distilled into the bomb, and 75 ml. of cold methylene chloride was injected through the bomb port with a hypodermic syringe. After 16.3 hr. at 69°, 34.2 g. of dark solid was washed out of the bomb with water. Sublimation at 80° and 0.2 mm. pressure of 10.0 g. of the dark solid gave 5.72 g. (85% yield) of 10,10-difluoroanthrone (IV), m.p. 130–149° dec., identified by comparison of its infrared spectrum with that of an analytical sample. An analytical sample, m.p. 141–142°, was prepared by several recrystallizations from cyclohexane followed by sublimation.

Anal. Calcd. for $C_{14}H_8F_2O$: C, 73.04; H, 3.50. Found: C, 72.97; H, 3.57.

The carbonyl absorption of IV occurred at 1677 cm.$^{-1}$ in the infrared (KBr disk). The n.m.r. spectrum had a multiplet cen-

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[1] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[2] L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 137.

[3] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962.

[4] Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3106 (1960).

[5] W. C. Smith, *ibid.*, **82**, 6176 (1960).

[6] (a) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

[7] Melting points are uncorrected. We thank P. McMahon, D. Johnson, and associates for the infrared spectra; O. Norton, D. Johnson, and associates for the n.m.r. spectra; and J. Nemeth and associates for the microanalyses. Details may be found in the Ph.D. thesis of R. Searle, University of Illinois, 1963.