NEW SYNTHETIC ROUTE FOR 2-CHLORO-1,3,2-DITHIASTIBOLANE INVOLVING A SKELETAL SUBSTITUTION REACTION

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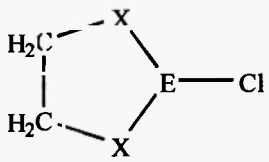
ABSTRACT

Herein we report the synthesis, characterization and conformational studies of 2-chloro-1,3,2-dithiastibolane **2**. Unexpectedly, treatment of 2-chloro-1,3,2-dithiaphospholane **1** with SbF_3 did not lead to the replacement of the chlorine of compound **1**. Instead, compound **2** was obtained in a rather high yield, *via* a skeletal substitution reaction. This is the first example of a skeletal substitution reaction involving the replacement of phosphorus by antimony. Compound **2** was characterized on the basis of ^1H and $^{13}C\{^1H\}$ NMR studies, mass spectroscopy and elemental analyses. A semi-empirical calculation of **2** was carried out and the results pointed to only one non planar conformation: a large half chair due to the size of antimony, which explains the magnetic equivalence of the four hydrogen atoms.

INTRODUCTION

A variety of compounds of type A have been reported and in general they have been prepared by treatment of the corresponding diol or dithiol with ECl_3 (E= As; P or Sb).



A { E = P; As; Sb ; X= O; Cl

1: E = P; X = S

2: E= Sb; X= S

The attempt to fluorinate 2-chloro-1,3,2-dithiaphospholane **1** with SbF_3, a well known fluorinate agent, gave an unprecedented skeletal substitution reaction, producing 2-chloro-1,3,2-dithiastibolane.

Few skeletal substitution reactions have been reported and to the best of our knowledge this is the first example involving the replacement of phosphorus by antimony. The first skeletal substitution reaction that has been reported by Abel and co-workers [1] showed the replacement of silicon atom of 2,2-diphenyl-1,3-dithia-2-silacyclopentane by boron, antimony or phosphorus on. Later Fagan *et al.*[2] described the exchange of zirconium by several main groups elements on metallacycle complexes and Cowley and co-authors [3] used the same approach to prepare a gallium heterocycle. More recently, Gates and Manners [4] reported the replacement of boron by arsenium or antimony on a boratophosphazene and claimed this to be the first example of this kind.

MATERIALS AND METHODS

All reactions were carried out either under dry dinitrogen in Schlenk tubes or by the use of high-vacuum techniques. Glassware was flame-dried in vacuum and solvents were dried, freshly distilled under dinitrogen, and degassed prior to use. The NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13 MHz for ^1H and 101.61 MHz for ^{13}C. All chemical shift data were recorded at 25°C and are quoted in δ, with positive values to high frequency with respect to $SiMe_4$ for ^1H and ^{13}C) and corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz. Microanalyses were performed on a Perkin Elmer 2400 CHN. Metal determinations were obtained by Atomic Absorption Spectroscopy using a Varian AAG and a Hitachi Z8200. The GC/MS was recorded on a HP5890 Series II/HP5989A Spectrometer. 2-chloro-1,3,2-dithiaphospholane **1** was prepared from the corresponding dithiol with PCl_3 and the details can be found in [5].

Synthesis of 2-chloro-1,3,2-dithiastibolane – To a solution of SbF_3 (1.13g, 6.3 mmol) in THF (50mL) was added 2-chloro-1,3,2-dithiaphosfolane (1g, 6.3 mmol). After 5 hours of stirring at room temperature, the mixture was evaporated to dryness and the light brown residue washed with hexane. Then, the main product

2-chloro-1,3,2-dithiastibolane was extracted with THF as a white solid; yield 0.76g (48%). This procedure was repeated at lower temperature (-5 ^{0}C to –25 ^{0}C) and a slight increase of the yield of the main product was observed (0.97g; 62%).
Analytical data for $C_2H_4ClS_2Sb$ **2** (PM = 284,76 g/mol); (calcd) :C(%):9.63, (10.90); H(%):1.63, (1.61); Sb(%):48.0, (51.5).
Mass Spectrum (EI,70eV;m/z): 250$[M]^+$; 221$[SbS_2Cl]^+$; 213$[SbS_2C_2H_4]^+$; 185$[SbS_2]^+$; 63$[S_2]^+$
^{1}H NMR data (400.13 MHz; $CDCl_3$): δ 3.77 (s; CH_2); $^{13}C\{^1H\}$ NMR data (101.61 MHz; $CDCl_3$): δ 43.1 (s).

RESULTS AND DISCUSSION

Unlike the 2-chloro-1,3,2-dioxaphospholane, its analogue, 2-chloro-1,3,2-dithiaphospholane **1**, does not undergo halogen exchange reaction by treatment with SbF_3 to yield 2-fluoro-1,3,2-dithiaphospholane [6]. Instead it undergoes a skeletal substitution reaction to yield 2-chloro-1,3,2-dithiastibolane **2**. There are only two well-known different reports of the preparation of **2**: (*i*) by treatment of 1,2-ethanedithiol with a HCl solution of $SbCl_3$ and (*ii*) by treatment of 2,2-dimethyl-1,3-dithia-2-silacyclopentane with $SbPhCl_2$[7].

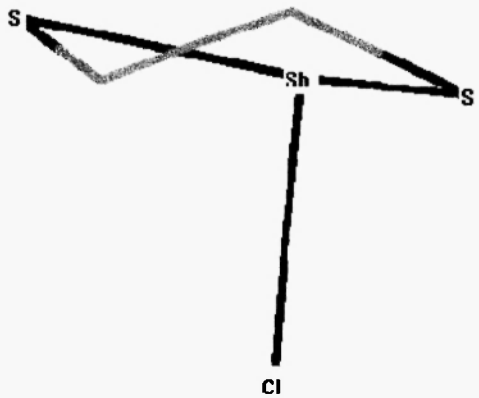


Fig 1 A lateral perspective of compound **2**

The characterization of **2** was based on its ^{1}H and ^{13}C NMR spectra, mass spectroscopy and elemental analyses. The mass spectrum of **2** shows the molecular peak at 250, with the pattern of lines typical of compounds containing chlorine. Its $^{13}C\{^1H\}$ NMR spectrum exhibits a singlet at δ43.1 and its ^{1}H NMR spectrum exhibits an unchangeable singlet at δ3.77 between -100^{0}C and 25^{0}C.

Table I: Main dihedral angles of the2-chloro-1,3,2-dithiastibolane.

Dihedral angle	Degrees
H(1)-C(5)-C(4)-H(9)	- 54.8
H(1)-C(5)-C(4)-H(10)	61.4
H(3)-C(5)-C(4)-H(9)	-171.0
H(3)-C(5)-C(4)-H(10)	-54.8
S(6)-C(5)-C(4)-S(8)	-61.1

This means that, unlike what has been observed in the case of its phosphorous analogue **1** [5], compound **2** has four equivalent hydrogen nuclei. That would not be in agreement with the solid state structure, which has been solved by X-ray crystal diffraction studies and shows that the ring is not planar[8]. Foster and co-workers [9] made the same observation about the ^{1}H NMR spectrum of **2**. However, in a previous work, Gates et al. [10], analyzing the ^{1}H NMR spectrum of **2**, suggested that either compound **2** is almost planar in solution or the large size of the Sb atom compared with the chloro-substituent masks the stereochemical effect of the later on the methylene protons [10].

We carried out a molecular geometric optimization employing the PM3 method, followed by a Osawa conformational search and a coordinated driving search trough the dihedral angles between the hydrogens. All the results pointed to only one stable conformer (ΔH^0_f = -13.9 kcal mol^{-1}; S^0= 93.9 cal mol^{-1} K^{-1}; μ = 2.8 Debye), which is a half-chair with a C_2 axis passing from the Sb to the middle of the C-C bond, with all the hydrogens equivalently spaced from the Sb atom (from 3.6 to 4.3 A) and at least 4 Å from the Cl atom, cf. Fig. 1, 2 and Table I. Therefore, the hydrogens would present a magnetic equivalence, a proposal which agrees with the ^{1}H NMR spectrum. Accordingly, our geometric optimization agrees with the hypothesis of Gates and coll.[10] that the 2-chloro-1,3,2-dithiastibolane **2** has a non planar conformation but their hydrogens present a magnetic equivalence due the size of the Sb atom and, consequently, of their distances to the Cl atom.

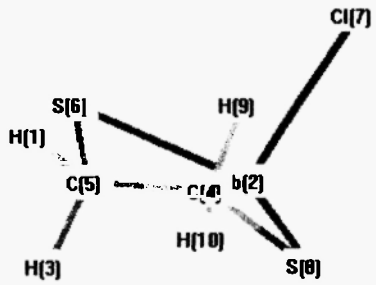


Fig 2 - A Newman projection of compound **2**

ACKNOWLEDGEMENT:

The authors thank FAPEMIG, FINEP, CNPq and PRPq-UFMG for the continuing support of this work.

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Received: March 23, 2001 - Accepted: May 2, 2001 –
Accepted in publishable format: May 7, 2001