

ORGANO GROUP VB CHEMISTRY

III. SYNTHESIS AND NMR SPECTRA OF SOME TERTIARY SUBSTITUTED ARYLSTIBINES AND ARYLBISMUTHINES

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SUMMARY

An improved method for the synthesis of some stibines and bismuthines of the general formula $(p\text{-XC}_6\text{H}_4)_3\text{E}$ and $(m\text{-XC}_6\text{H}_4)_3\text{E}$ ($\text{X}=\text{Cl}$ or F , $\text{E}=\text{Sb}$ or Bi) is described.

^1H and ^{19}F NMR spectra are recorded for various compounds, and the results of a partial analysis of the NMR spectra are reported.

INTRODUCTION

In previous papers^{1,2} the synthesis and the vibrational spectra of some tertiary substituted arylarsines have been described. These compounds, together with the new ones presented here, have subsequently been used as ligands in transition metal carbonyl chemistry³.

SYNTHESIS

a. $(4\text{-FC}_6\text{H}_4)_3\text{Sb}$, $(3\text{-FC}_6\text{H}_4)_3\text{Sb}$, $(4\text{-ClC}_6\text{H}_4)_3\text{Sb}$ and $(3\text{-ClC}_6\text{H}_4)_3\text{Sb}$

These compounds were prepared using the general method reported elsewhere¹. The procedure is described here only for $(4\text{-FC}_6\text{H}_4)_3\text{Sb}$; the other stibines are obtained in a similar manner.

$4\text{-FC}_6\text{H}_4\text{Br}$ (0.5 mole), dissolved in dry ether was added dropwise to 12.5 g Mg turnings at 0° . The resulting Grignard solution was cooled to -12° and 22.82 g SbCl_3 dissolved in dry ether slowly added. This mixture was stirred for an additional hour at room temperature and after completion of the reaction was treated with a saturated NH_4Cl solution. The ether layer was separated and dried over Na_2SO_4 . The solvent was then evaporated from the solution *in vacuo* and the residue recrystallized from ethanol. Further purification was obtained by distilling the crude product under high vacuum.

All operations were undertaken in a protective nitrogen atmosphere.

b. $(4\text{-FC}_6\text{H}_4)_3\text{Bi}$, $(3\text{-FC}_6\text{H}_4)_3\text{Bi}$, $(4\text{-ClC}_6\text{H}_4)_3\text{Bi}$ and $(3\text{-ClC}_6\text{H}_4)_3\text{Bi}$

The same procedure as described for the corresponding stibium derivatives

TABLE 1

ANALYTICAL AND PHYSICAL DATA OF SUBSTITUTED PHENYL-STIBINES AND -BISMUTHINES

Compound	Yield (g)	M.p. (°C)	Analysis found (calcd.) (%)		Mol. wt. found (calcd.)
			C	H	
(4-F-C ₆ H ₄) ₃ Sb	28.0	91.8	53.87 (53.11)	2.78 (2.97)	403.1 (407.0)
(3-F-C ₆ H ₄) ₃ Sb	32.0	34.3	52.74 (53.11)	2.96 (2.97)	409.0 (407.0)
(4-Cl-C ₆ H ₄) ₃ Sb	34.9	111.5	46.91 (47.37)	2.56 (2.65)	451.4 (456.4)
(3-Cl-C ₆ H ₄) ₃ Sb	39.0	53.7	47.25 (47.37)	2.79 (2.65)	463.9 (456.4)
(4-F-C ₆ H ₄) ₃ Bi	37.2	92.4	43.37 (43.74)	2.53 (2.45)	502.3 (494.3)
(3-F-C ₆ H ₄) ₃ Bi	40.9	69.0	43.62 (43.74)	2.39 (2.45)	491.1 (494.3)
(4-Cl-C ₆ H ₄) ₃ Bi	45.9	115.4	39.53 (39.77)	2.26 (2.23)	543.5 (543.6)
(3-Cl-C ₆ H ₄) ₃ Bi	46.3	61.5	39.11 (39.77)	2.41 (2.23)	551.0 (543.6)

was used. Because of the small solubility of BiCl₃ in ether, however, a refluxing BiCl₃/ether suspension was pumped under N₂ into the Grignard solution.

The analytical and physical data of the compounds are presented in Table 1.

MAGNETIC RESONANCE SPECTRA

a. Proton magnetic resonance spectra

The spectra of (4-FC₆H₄)₃Sb and of (4-FC₆H₄)₃Bi are in agreement with the theoretical spectral pattern expected for AA'XX' systems, as discussed by Garbish⁴. A similar pattern was observed for (4-FC₆H₄)₃As and (4-FC₆H₄)₃AsO¹. The analysis of these spectra could therefore be performed in a similar way as for the arsine derivatives. The results of the analysis are summarized in Table 2.

TABLE 2

Assignment	(4-FC ₆ H ₄) ₃ Sb	(4-FC ₆ H ₄) ₃ Bi
δH _o	+7.31 ^a	+7.64 ^a
δH _m	+6.95	+7.00
³ J(H _o -H _m)	8.3 ^b	8.3 ^b
⁴ J(H _o -H _{o'})	2.1	2.1
⁴ J(H _m -H _{m'})	2.1	2.1
⁵ J(H _o -H _{m'})	0.3	0.3
³ J(¹⁹ F-H _m)	8.8	8.8
⁴ J(¹⁹ F-H _o)	6	6

^a δ values are given in ppm relative to TMS as a standard. ^b J values are given in Hz.

The PMR spectrum of $(4\text{-ClC}_6\text{H}_4)_3\text{Sb}$ consists of only one peak. The ^{123}Sb NQR frequency is observed at 92.20 MHz⁵; this resonance could serve as a very efficient decoupler and might cause peak broadening and collapse of spin multiplets.

For $(4\text{-ClC}_6\text{H}_4)_3\text{Sb}$ it was found that $\delta = +7.26$ ppm.

The PMR spectrum of $(4\text{-ClC}_6\text{H}_4)_3\text{Bi}$ consists of a broad AB type quadruplet. Here again quadrupole broadening through the presence of the quadrupolar Bi nucleus may be responsible for the poor resolution observed. The analysis yields for $(4\text{-ClC}_6\text{H}_4)_3\text{Bi}$: $\delta\text{H}_o = +7.54$ ppm, $\delta\text{H}_m = +7.27$ ppm, $^3J(\text{H}_o\text{-H}_m) = 8$ Hz.

The PMR spectra of the *meta*-substituted phenylstibines and bismuthines consist of a very complex pattern of peaks and for this reason only the chemical shift corresponding to the center is given. $(3\text{-FC}_6\text{H}_4)_3\text{Sb}$: $\delta_c = +7.16$ ppm, $(3\text{-FC}_6\text{H}_4)_3\text{Bi}$: $\delta_c = +7.37$ ppm, $(3\text{-ClC}_6\text{H}_4)_3\text{Sb}$: $\delta_c = +7.28$ ppm, and $(3\text{-ClC}_6\text{H}_4)_3\text{Bi}$: $\delta_c = +7.40$ ppm. The spectrum of $(3\text{-ClC}_6\text{H}_4)_3\text{Sb}$ is also broadened (NQR = 92.96 MHz)⁵. The chemical shift value is taken as positive for a higher frequency.

b. Fluorine-19 magnetic resonance spectra

The spectra of $(4\text{-FC}_6\text{H}_4)_3\text{Sb}$ and $(4\text{-FC}_6\text{H}_4)_3\text{Bi}$ consist of a triplet of triplets similar to those reported for the analogous arsenic compounds. The parameters obtained are tabulated in Table 3.

TABLE 3

Compound	Solvent	δ^a	$^3J(^{19}\text{F-H}_m)^b$	$^4J(^{19}\text{F-H}_o)$
$(4\text{-FC}_6\text{H}_4)_3\text{Sb}$	CCl_4	-112.3	6	8.8
	C_6H_6	-111.9	6.1	9
$(4\text{-FC}_6\text{H}_4)_3\text{Bi}$	CCl_4	-113	6	8.8
	C_6H_6	-112.6	6.1	9.1
Compound	Solvent	δ^a	$^3J(^{19}\text{F-H}_o)^c$	$^4J(^{19}\text{F-H}_m)$
$(3\text{-FC}_6\text{H}_4)_3\text{Sb}$	C_6H_6	-111.5		
	CCl_4	-111.8	8	5
	$(\text{CH}_3)_2\text{CO}$	-111.7	8	5
$(3\text{-FC}_6\text{H}_4)_3\text{Bi}$	C_6H_6	-111.5		
	CCl_4	-111.8	8.4	5.6
	$(\text{CH}_3)_2\text{CO}$	-111.7	8.4	5.6

^a δ values are given in ppm relative to CCl_3F : the sign being taken as negative for a lower frequency.

^b J values are given in Hz. ^c H_o and H_m represent the protons in the *ortho* or *meta* positions relative to fluorine.

For $(3\text{-FC}_6\text{H}_4)_3\text{Sb}$ and $(3\text{-FC}_6\text{H}_4)_3\text{Bi}$, benzene, acetone and carbon tetrachloride were used as solvents. The results of a tentative analysis for the *meta*-fluoro-substituted phenylstibines and bismuthines, dissolved in acetone and carbon tetrachloride, are given in Table 3.

c. Experimental

A Bruker-Physik HF-X5 spectrometer, operating at 90 MHz was used to record the PMR spectra. The ^{19}F spectra were obtained on the same instrument at

84.66 MHz. Carbon tetrachloride was used as solvent throughout for the determination of PMR spectra. Other solvents (as indicated) were only used for the determination of the fluorine magnetic resonance spectra. TMS and C_6F_6 were used as reference solvents and to actuate the field frequency stabilisation of the spectrometer.

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