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I. SYNTHESIS AND NMR SPECTRA OF SOME TERTIARY SUBSTITUTED ARYLARSINES AND ARSINE OXIDES

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SUMMARY

Improved methods for the synthesis of some arsines of general formulae $(p\text{-}XC_6H_4)_3As$ and $(m\text{-}XC_6H_4)_3As$ (X = Cl, or F), and of their corresponding oxides, are described.

The ^1H and ^{19}F NMR spectra are presented for some of these compounds, and the results of a partial analysis of the NMR spectra reported.

INTRODUCTION

In a previous paper[1] the synthesis of several arylphosphines was described, and of these compounds tris(*p*-fluorophenyl) phosphine has subsequently been used as a ligand in several transition metal carbonyl complexes[2,3]. In this study the synthesis of the analoguous arsines and oxides has been undertaken.

SYNTHESIS

(*a*). $(4\text{-}FC_6H_4)_3As$, $(3\text{-}FC_6H_4)_3As$, $(4\text{-}ClC_6H_4)_3As$ *and* $(3\text{-}ClC_6H_4)_3As$

These compounds were prepared by a general procedure developed in this laboratory[1]. The method as described below is for $(4\text{-}F\text{-}C_6H_4)_3As$; the other arsines have been obtained in a similar manner.

$4\text{-}FC_6H_4Br$ (0.5 mole), dissolved in dry ether, was added dropwise to 12.5 g of Mg turnings at 0°C. The Grignard solution was cooled to $-12°$ and 11 ml of $AsCl_3$ dissolved in 50 ml ether slowly added. After completion of the reaction, the mixture was treated with a saturated NH_4Cl solution, the ether layer separated and dried over Na_2SO_4, and evaporated *in vacuo*, the residue being recrystallized from ethanol. All operations were undertaken in a protective nitrogen atmosphere.

(*b*). $(4\text{-}FC_6H_4)_3AsO$, $(3\text{-}FC_6H_4)_3AsO$, $(4\text{-}ClC_6H_4)_3AsO$ *and* $(3\text{-}ClC_6H_4)_3AsO$

Yakovleva *et al.*[4] have prepared diphenyl-*m*-tolylphosphine oxide by oxidation of the corresponding phosphine using H_2O_2. This procedure has now been improved to allow the preparation of the arsine derivatives in the following manner.

H_2O_2 (3 ml 30%) was added dropwise to a solution of 0.005 moles of $(4\text{-}FC_6H_4)_3As$ in 50 ml acetone. The mixture was refluxed for 1 h, the solvent evaporated *in vacuo* and the residue dissolved in a minimum amount of benzene. 10 ml of 0.25 *N* NaOH was then added to the benzene solution to decompose the unreacted H_2O_2, the benzene layer separated and dried over Na_2SO_4, and evaporation *in vacuo* of the dried solution yielded the pure product. The other arsine oxides were prepared using the same method.

Analytical and physical data relating to the synthetized compounds are presented in Table 1.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SUBSTITUTED PHENYLARSINES AND ARSINE OXIDES

Compound	Yield (g)	M.p. (°C)	Analysis (%)		Mol. Wt.
			C	H	
$(4\text{-}FC_6H_4)_3As$	32.0	74.0	60.06 (60.02)	3.30 (3.36)	351.4 (360.2)
$(3\text{-}FC_6H_4)_3As$	38.0	41.0	59.01 (60.02)	3.41 (3.36)	351.4 (360.2)
$(4\text{-}ClC_6H_4)_3As$	33.3	105.4	51.97 (52.73)	2.90 (2.95)	400.7 (409.6)
$(3\text{-}ClC_6H_4)_3As$	32.3	73.3	51.94 (52.73)	2.98 (2.95)	402.5 (409.6)
$(4\text{-}FC_6H_4)_3AsO$	1.4	159.0	57.36 (57.41)	3.36 (3.21)	
$(3\text{-}FC_6H_4)_3AsO$	1.5	187.0	56.94 (57.41)	3.16 (3.21)	
$(4\text{-}ClC_6H_4)_3AsO$	1.3	205.1	51.02 (50.75)	2.75 (2.84)	
$(3\text{-}ClC_6H_4)_3AsO$	1.4	163.2	50.34 (50.75)	2.91 (2.84)	

[a] The values in brackets correspond to the calculated C and H analysis, and the theoretical molecular weight respectively.

MAGNETIC RESONANCE SPECTRA

(*a*). *Proton magnetic resonance spectra*

The spectra of $(4\text{-}FC_6H_4)_3As$ and $(4\text{-}FC_6H_4)_3AsO$ are shown in Fig. 1 and 2 respectively. By comparison with theoretical spectral patterns for AA'XX' systems, as discussed by Garbisch[5], these spectra may be considered as consisting of two AA'XX' subsprectra by coupling to ^{19}F. The group lying towards low field strenghts is believed to represent the resonance of the protons in the *ortho* position with respect to arsine while the spectrum of the *meta* protons, although similar to that of the *ortho* protons, is more overlapping due to the value of $^3J(^{19}F\text{–}H_m)$. The results of the analysis according to Garbisch are summarized in Table 2.

Although the NMR spectra of $(4\text{-}ClC_6H_4)_3As$ and $(4\text{-}ClC_6H_4)_3AsO$ should have the appearance of a AA'BB' type multiplet pattern, only a type AB quadruplet

(*Continued* on p. 221)

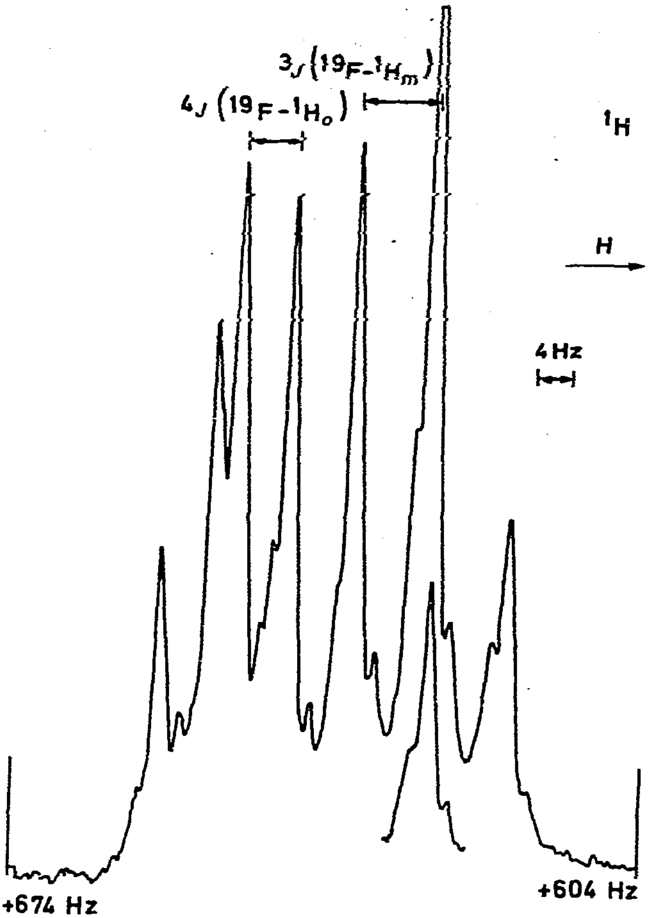

Fig. 1. ^{1}H NMR spectrum of $(4\text{-}FC_6H_4)_3As$ (δ in Hz relative to TMS).

TABLE 2

Compound	$(4\text{-}FC_6H_4)_3As$	$(4\text{-}FC_6H_4)_3AsO$
$\delta(H_o)$	7.20[a]	7.77[a]
$\delta(H_m)$	7.00	7.22
$^3J(H_o\text{-}H_m)$	8.1[b]	8.3[b]
$^4J(H_o\text{-}H_{o'})$	2.3	2.4
$^4J(H_m\text{-}H_{m'})$	2.3	2.4
$^5J(H_o\text{-}H_{m'})$	0.4	0.3
$^3J(^{19}F\text{-}H_m)$	8.6	8.7
$^4J(^{19}F\text{-}H_o)$	5.8	5.5

[a] δ values are given in ppm. [b] J values are given in Hz.

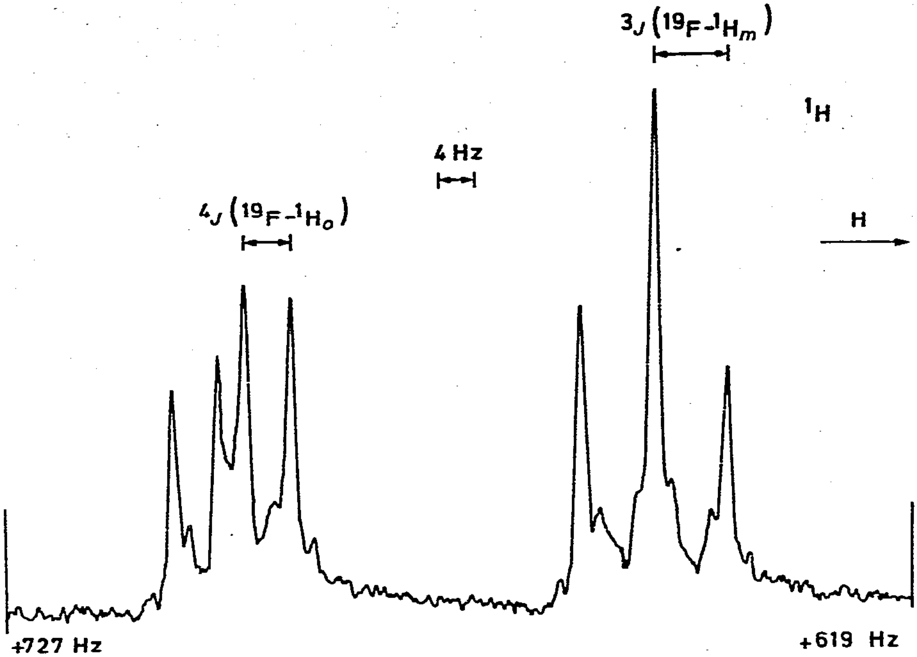

Fig. 2. ^{1}H NMR spectrum of $(4\text{-}FC_6H_4)_3AsO$ (δ in Hz relative to TMS).

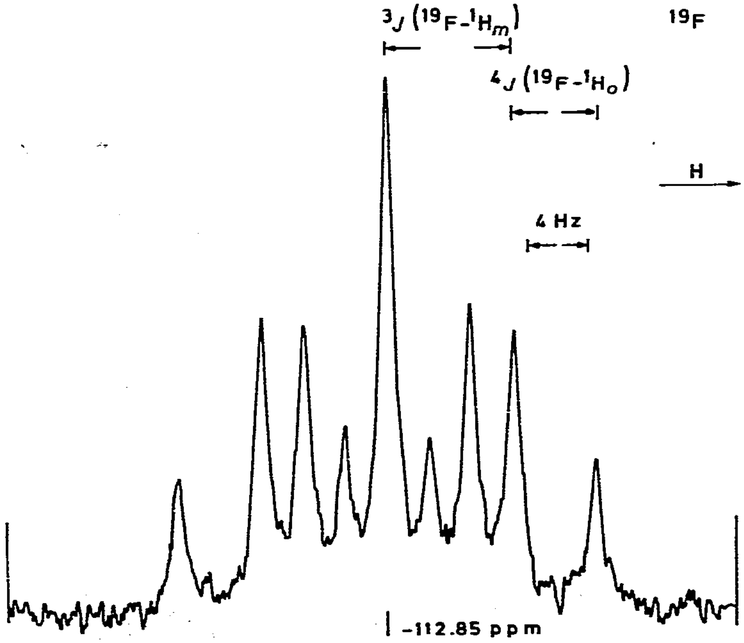

Fig. 3. ^{19}F NMR spectrum of $(4\text{-}FC_6H_4)_3As$ (δ in ppm relative to CCl_3F).

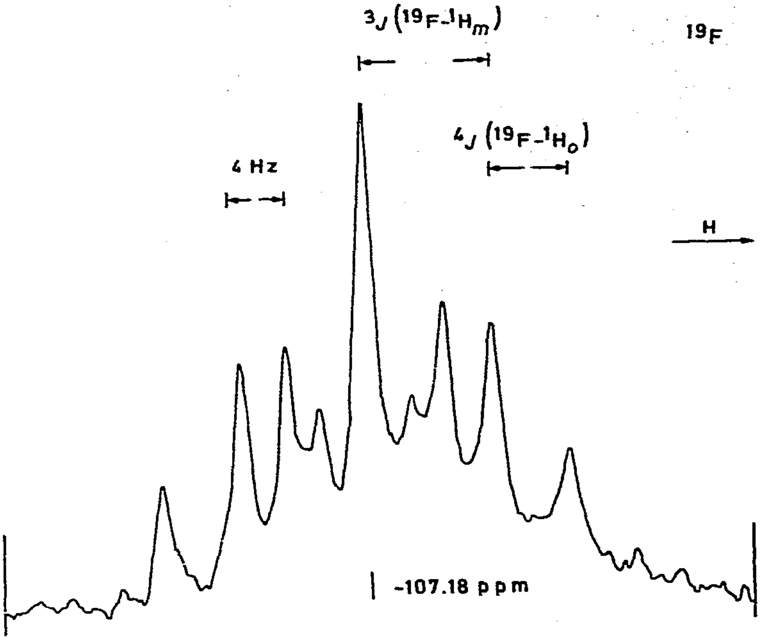

Fig. 4. ^{19}F NMR spectrum of (4-$FC_6H_4)_3AsO$ (δ in ppm relative to CCl_3F).

could be resolved. Starting from this assumption, a tentative analysis yields for (4-$ClC_6H_4)_3As$: $\delta(H_o)$ 7.28 ppm, $\delta(H_m)$ 7.18 ppm, $^3J(H_o\text{–}H_m)+{}^5J(H_o\text{–}H_{m'})=8.8$ Hz; and for (4-$ClC_6H_4)_3AsO$: $\delta(H_o)$ 7.82 ppm, $\delta(H_m)$ 7.65 ppm, $^3J(H_o\text{–}H_m)+{}^5J(H_o\text{–}H_{m'})=$ 8.8 Hz.

The NMR spectra of the *meta*- substituted phenylarsines and arsine oxides consist of a very complex pattern of peaks and only the chemical shifts of the center are given. (3-$FC_6H_4)_3As$: δ_c 7.13 ppm. (3-$FC_6H_4)_3AsO$: δ_c 7.53 ppm. (3-$ClC_6H_4)_3As$: δ_c 7.18 ppm. (3-$ClC_6H_4)_3AsO$: δ_c 7.72 ppm.

The sign of the chemical shift is taken as positive for a higher frequency.

(*b*). ^{19}*F Magnetic resonance spectra*

The spectra of (4-$FC_6H_4)_3As$ and (4-$FC_6H_4)_3AsO$, as presented in Fig. 3 and 4, consist of a triplet of triplets. The parameters obtained are tabulated in Table 3.

Only solutions of (3-$FC_6H_4)_3As$ in CCl_4 and in $(CH_3)_2CO$ as solvents yielded good resolved spectra. In benzene the spectrum consists of a complex pattern of peaks, probably due to solvent interaction, and for this reason only the spectrum of (3-$FC_6H_4)_3As$ in $(CH_3)_2CO$ is shown in Fig. 5. With solutions of (3-$FC_6H_4)_3AsO$ in benzene a double triplet structure appears, as expected. The results of a tentative analysis for the *meta* fluoro-substituted phenylarsines and arsine oxides are given in Table 3.

(*c*). *Experimental*

A Bruker-Physik HF-X5 spectrometer, operating at 90 MHz, was used to record the NMR spectra, the ^{19}F spectra being obtained on the same instrument at 84.66 MHz. Carbon tetrachloride was used as solvent throughout for the arsines, and acetone for the arsine oxides. Other solvents were only used for the *meta* fluoro-sub-

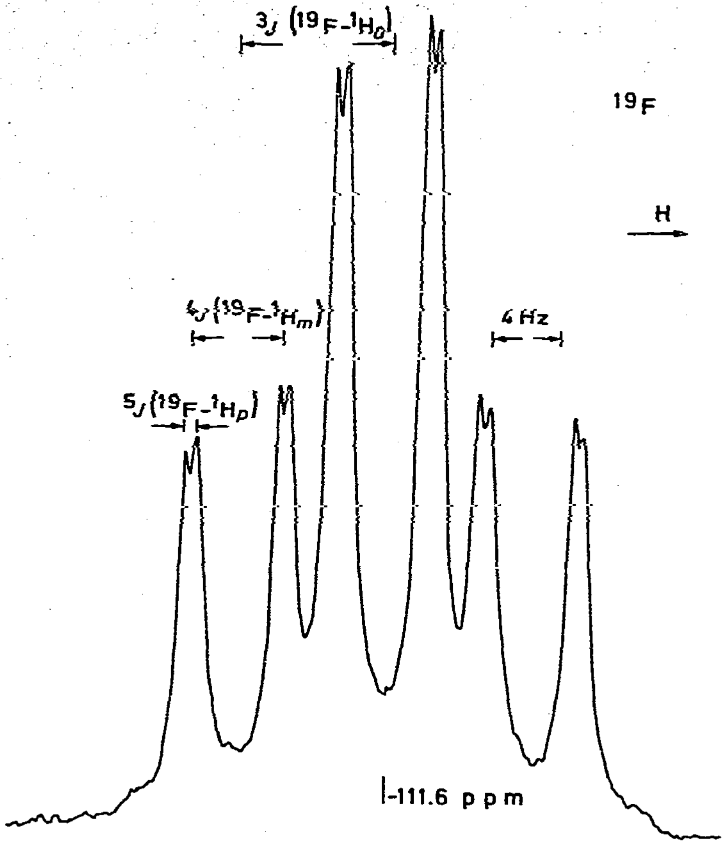

Fig. 5. ^{19}F NMR spectrum of $(3\text{-}FC_6H_4)_3As$ (δ in ppm relative to CCl_3F).

TABLE 3

Compound	Solvent	δ^a	Coupling constants		
			$^3J(^{19}F\text{-}H_m)^b$	$^4J(^{19}F\text{-}H_o)$	
$(4\text{-}FC_6H_4)_3As$	CCl_4	−112.8	8.6	5.8	
$(4\text{-}FC_6H_4)_3AsO$	$(CH_3)_2CO$	−107.2	8.7	5.5	
			$^3J(^{19}F\text{-}H_o)^c$	$^4J(^{19}F\text{-}H_m)$	$^5J(^{19}F\text{-}H_p)$
$(3\text{-}FC_6H_4)_3As$	C_6H_6	−111.5			
	CCl_4	−111.8	8.4	5.6	
	$(CH_3)_2CO$	−111.6	8.7	5.5	0.5
$(3\text{-}FC_6H_4)_3AsO$	C_6H_6	−109.3			
	$(CH_3)_2CO$	−109.6	8	5.9	

[a] Shifts in ppm relative to CCl_3F. The sign is taken as negative for lower frequency.
[b] Couplings are given in Hz. [c] H_o, H_m, H_p represent the positions of the protons with respect to fluorine.

stituted phenyl compounds. TMS and C_6F_6 were used as reference liquids and to actuate the field frequency stabilisation circuits of the spectrometer.

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