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THE TAFT σ_I CONSTANTS OF SOME PHOSPHORYLOXY SUBSTITUENTS.

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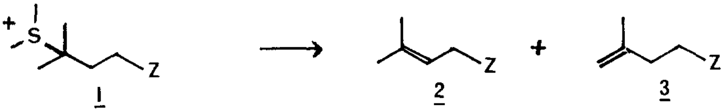
Abstract : The Taft's constants of some phosphoryloxy groups were measured by fluorine NMR spectroscopy.

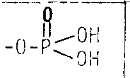
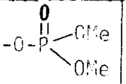
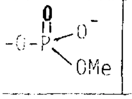
In previous work on the chemical factors governing the biosynthesis of geranyl (or farnesyl) pyrophosphate, it has been shown that the terminal group Z in sulfonium salts 1 has a strong influence on the direction of elimination (under basic conditions) leading to the "natural" 2, or the retro 3 elimination products. When Z was a dimethylphosphoric ester residue $OPO(OMe)_2$ the elimination gave almost exclusively the natural product 2, the methyl hydrogen phosphoric ester was a little less selective [1]. With other groups Z, widely varying results were obtained : from 1 to 93% natural isomer in the mixture. A fairly good correlation was found between the proportion of natural isomer formed and the electron attracting effect of the Z group [2a,2b] as expressed for instance by Taft's σ_I coefficients. With a "bad" leaving group such as dimethylsulfide the relative acidities of the various protons govern the direction of elimination as in the well known Hofmann rule [2c]. Examination of the literature showed however that the σ_I values of phosphoric esters were not known. In view of the importance of phosphoric esters, we endeavoured to measure these values for the dimethoxyphosphoryloxy $-O-PO(OMe)_2$, methoxyhydroxyphosphoryloxy (mono anion) $-O-PO(O^-)(OMe)$ and dihydroxy phosphoryloxy $-O-PO(OH)_2$.



A very convenient method uses the fluorine nuclear magnetic resonance shielding in meta- substituted fluorobenzenes 5 compared with that of fluorobenzene (see 3[c] and references cited therein). The necessary compounds were prepared by known methods. m-Fluorophenyl dihydrogen phosphate 5a was prepared from phosphorus pentachloride and m-fluorophenol [6]. Sodium m-fluoro phenoxide was treated with dimethylphosphorochloridate [4] in ether to give dimethyl m-fluorophenyl phosphate 5b ; this was mono demethylated by sodium thiophenoxide in DMF [5] to give sodium methyl m-fluorophenyl phosphate 5c [7].

Fluorine chemical shift measurements were made using Taft's procedure [3c]. The approach was checked with a number of m-fluorobenzenes 5,X=NO_2, NH_2,OH of known σ_I values-(Table 1). A fair linear correlation (Fig.1) of intramolecular shielding produced by meta substituents with σ_I values was obtained except for X=H, consistent with the results of Taft, eq.1 : $\delta^{PhF}(m\text{-}PhFX) = 8.16\ \sigma_I - 1.51$.

TABLE I : ^{19}F chemical shift in meta substituted fluorobenzene 5 with respect to fluorobenzene.

X	δ^{PhF}_{mPhFX}	δ^{PhF}_{mPhXF} a)	σ_I	σ_I a)
$-NO_2$	3.64	3.6		0.63
-OH	0.50	0.43		0.25
$-NH_2$	-0.68	-0.78		0.10
 $-O-P(=O)(OH)_2$	3.74		0.64	
 $-O-P(=O)(OMe)_2$	2.98		0.55	
 $-O-P(=O)(O^-)(OMe)$	1.04		0.31	

a) Ref.3c : chemical shift measured in 5% (vol.) solution of 5, 2%(vol.) 1,1,2,2-tetrafluoro 3,3,4,4-tetrachlorocyclobutane in methanol, 27°C. σ_I value given by Taft for weakly protonic solvents.

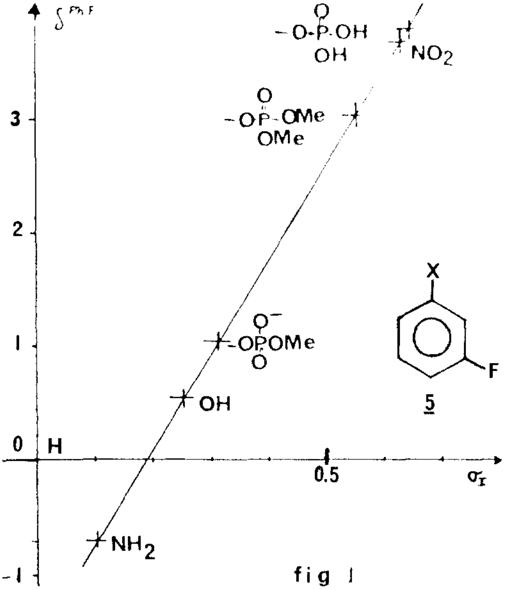


fig 1

In ppm downfield from internal reference fluorobenzene ; 3% (w/w) solutions for 5, 1.5% (w/w) of fluorobenzene in methanol-d_4, 21°C.

The fluorine chemical shifts of compounds 5 abc were then measured and the σ_I values for dihydroxyphosphoryloxy, dimethoxyphosphoryloxy and methoxyoxyphosphoryloxy groups were determined from figure 1 and are listed in Table 1. It will be seen from the results that the determined Taft σ_I constants depend to a large extent on the substituents and the charges to be found on the phosphonated oxygen atoms. Interestingly, it was found that the neutral groups have very high σ_I values (cf NO_2:0.63 ; NH_3^+ : 0.60 ; CN:0.56).

REFERENCES

1) L. Jacob, M. Julia, B. Pfeiffer and C. Rolando, Tetrahedron Lett., 24, 4327 (1983). 2) a) B. Badet, M. Julia, J.M. Mallet and C. Schmitz, ibid, 4331 ; b) paper submitted to Tetrahedron ; c) J.F.Bunnett, Survey of Progress in Chemistry, 5, 53 (1969). 3) a) M. Charton, J. Org. Chem., 29, 1222 (1964) ; b) G.B. Barlin and D.D. Perrin, Quat. Rev. 20, 75 (1966) ; c) R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.F. Andersen and G.T. Davis, J. Am. Chem. Soc., 95, 709-722 (1963). 4) J.I.G. Cadogan and L.C. Thomas, J. Chem. Soc. 2248 (1968). 5) P. Savignac and G. Lavielle, Bull. Soc. Chim. Fr., 1506 (1974). 6) J.D. Chanley, E.M. Gindler and H. Sobotka, J. Am. Chem. Soc., 74, 4347 (1952). 7) Preparation of phosphoric esters and spectroscopic data : 5a yield 50%; ^{1}HNMR 250MHZ $CDCl_3$/TMS 7.38,q,1H(J=8Hz) ; 7.15-6.9,m,3H. 5b yield 80%; $BP_{0.5}$ 94°C ; ^{1}HNMR 250MHz $CDCl_3$/TMS 7.35,q,1H,J= 8Hz; 7.1-6.9,m, 3H ; 3.9,d,6H,J_{PH}=12Hz. Mass spectrum : 220,125,112,109,108. 5c yield 50% ; MP(CH_3 $COCH_3$/ ipr_2O) ; 172°C ; ^{1}HNMR 250MHz, DMSO/TMS : 7.2,q,8Hz,1H ; 7.0,dt,12Hz,2Hz,1H ; 6.9,m,1H ; 6.7,td,8Hz,2Hz ; 3.35,d,11Hz,3H. 8) Our thanks are due to Dr Besace for recording the ^{19}F NMR spectra on his Bruker 250MHz machine.

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