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PROTONATION OF PHOSPHINAMIDES: THE COUPLING CONSTANT CRITERIA FOR O *VS* N PROTONATION[1]

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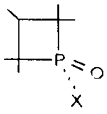
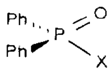
The suggestion has been made[2] that the most stable form of protonated phosphinamides has the proton on nitrogen rather than on the phosphoryl oxygen. Among other evidence, the coupling constant, J_{PNCH}, was observed to decrease upon protonation of two different phosphinamides, **1b** and **2b**. This is in contrast to the observed increase in the coupling constant, J_{POCH}, when the corresponding phosphinate esters, **1a** and **2a**, are protonated on oxygen. The possibility of using this coupling constant behavior as a general criteria for establishing the position of protonation of phosphinamides was proposed. We have had occasion to synthesize a number of compounds which can serve as models for O-protonation and thus provide a test for this coupling constant criteria; namely, phosphoryl oxygen alkylated phosphonium salts, **4**, **5**, and **6**.



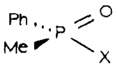
1a X = OMe

1b X = NMe_2



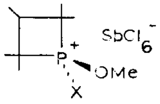
2a X = OMe

2b X = NMe_2



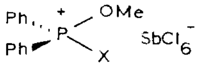
3a X = OMe

3b X = NMe_2

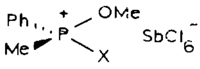


4a X = OMe

4b X = NMe_2



5a X = OMe



6a X = OMe

6b X = NMe_2

The synthesis of the phosphonium salts[3] was readily accomplished by O-alkylation[4] of the corresponding phosphoryl compounds, **1**, **2**, and **3**. The table lists the coupling constants (J) and chemical shifts (δ) of the respective ligands. All spectra were run in the same solvent (CH_2Cl_2), except where noted,[5] and under similar concentrations (ca. 20%).

	X = OCH_3		X = NMe_2	
Compound	$\delta(POC\underline{H}_3)$	J_{POCH}	$\delta(PNC\underline{H}_3)$	J_{PNCH}
1	3.75	10.0	2.53	10.2
Protonated **1**[a]	---	10.7[b]	---	7.9[b]
4	4.25, 4.29	10.8, 10.8	2.97	10.0
2	3.73	11.1	---	11.1[a]
Protonated **2**[a]	---	12.1[b]	---	10.0[b]
5	4.03[c]	12.0	---	---
3	3.59	11.5	2.60	10.7
Protonated **3**	---	12.1[b]	---	---
6	4.18	12.0	3.00	10.8

[a] Reference 2. [b] Solvent H_2SO_4 [c] Acetone-d_6

The increase in J_{POCH} reported for protonation of the phosphinate esters **1a**, **2a**, and **3a** is similar to that observed upon O-alkylation, supporting the model. Furthermore, the J_{PNCH} which decreased upon protonation of **1b** and **2b** remains virtually constant upon phosphoryl oxygen alkylation, **4b** and **6b**, consistent with the original postulate[2] that these phosphinamides are protonating on nitrogen. The observation that J_{PNCH} does not increase upon O-alkylation, however, renders the use of a change in coupling constant as a criteria for O vs N protonation questionable if a small decrease is observed upon protonation.

REFERENCES

1. This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society and an FIC Grant from Colorado State University.

2. P. Haake and T. Koizumi, Tetrahedron Letters, 4850 (1970).

3. All phosphonium salts gave satisfactory elemental analyses and had nmr spectra consistent with prediction.

4. H. Meerwein, E. Brattenberg, H. Gold, E. Pfeil, and G. Willfang, J. Prakt. Chem., **154**, 83 (1939).

5. The J_{PNCH} for **1b** was constant in other solvents such as CH_3Cl, acetone, nitromethane, and methanol.