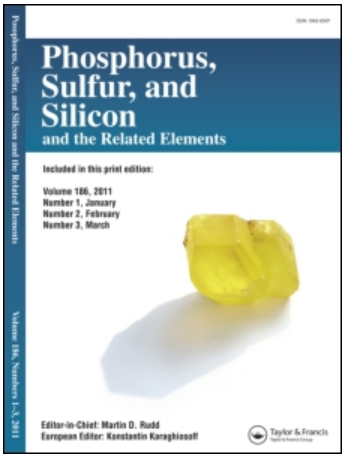

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Alkylation and H-D Exchange of Tetraazathiapentalenes Fused with Pyrimidine and/or Pyridine Ring

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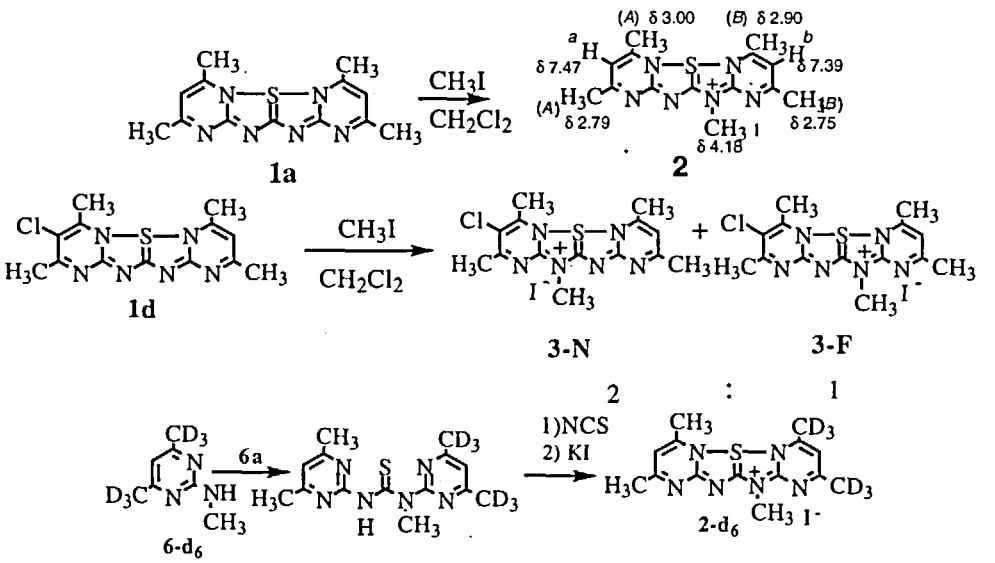
Selectivity of alkylation of and that of deuteration of methyl groups attached to the pyrimidine ring of tetraazathiapentalenes are discussed.

INTRODUCTION

Tetraazathiapentalenes **1** fused with pyrimidine rings are analogoues of thiathiophthene and the essential feature of the molecule is the presence of hypervalent N-S-N bond. The character of the hypervalent bond is highly susceptible to slight difference of electron-withdrawing abililty of the two nitrogens induced by the substituent at the pyrimididne ring.

RESULTS AND DISCUSSION

Methylation of symmetric **1a** afforded **2** exclusively. Methylationof unsymmetric **1d** gave **3-N** and **3-F** in a ratio of 2:1, selectively. The structure of products were determined by independent synthesis such as shown below.



The deuteration of the methyl groups attached to the pyrimidine ring of **1** and **2** and related compounds were carried out ^1H NMR spectroscopically in CD_3OD solution at 80 C under pseudo-first-order conditions. The kinetic study was carried out at the same concentration ($1.36x10^{-2}$ mol/L) until one half-life. The rate constants are shown in TABLE 1. The deuterium exchange rates are very sensitive to the electronic properties of the heterocycle opposed to the dimethylpyrimidine ring.

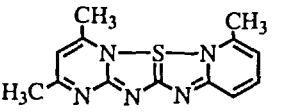
The deuteration of a pair of the methyl groups (A and A' or B and B') in the same pyrimidine ring proceeded by the same rate constants. This phenomenon must resultfrom the very much faster position-exchange (rotation: 10^{-2} s^{-1}) of the methyl groups relative to the isotope exchange ($k=10^{-4}$ 10^{-5} s^{-1}).

It is noticeable that the methyl hydrogens (A and A') underwent the isotope exchange 6.2-6.8 times as fast as the methyl hydrogens (B and B') near the thiadiazolium part in **2**. The result indicates that the positive charge in **2** is more delocalized into the pyrimidine ring of the A,A'-side compared with the other primidine ring of the B,B'-side which is closer to the thiadiazolium site. This is consistent with the chemical shift s of the methyl groups in the ^1H NMR spectrum. As expectedly, the siotope exchange reaction rate in the monocationic **2** is 10 times faster than that of the neutral **1**.

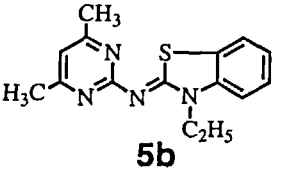
TABLE 1

Reaction Rate Constants of Deuterium Exchange of the Methyl Hydogens in **1a**, **2**, **4b**, and **5b**

compd	solvent[a]	k_A, $k_{A'}$ (s^{-1})	k_B, $k_{B'}$ (s^{-1})
1a	B	$1.5x10^{-5}$	
4b	B	$1.7x10^{-6}$	
2	A	$2.4x10^{-5}$	$3.5x10^{-6}$
2	B	$4.3x10^{-4}$	$6.9x10^{-5}$
5b	A	$1.6x10^{-6}$	
5b	B	$1.5x10^{-6}$	



4b



5b

[a] Solvent: A; CD_3OD, B; $CD_3OD/CDCl_3$ (volume ratio is 1 : 1).
Conditions: at 80 °C in $1.36x10^{-2}$ mol/l solution for each substance.

REFERENCES

1. K. Ohkata, M. Ohsugi, K. Yamamoto, M. Ohsawa, and K.-y. Akiba, *J. Am. Chem. Soc.*, **118**, in press (July) (1996).