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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Akiba, Kin-Ya , Yamamoto, Kazuhiro , Ohsawa, Mika and Ohkata, Katsuo(1997) 'Alkylation and H-D Exchange of Tetraazathiapentalenes Fused with Pyrimidine and/or Pyridine Ring', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 120: 1, 427 — 428

To link to this Article: DOI: 10.1080/10426509708545581

URL: <http://dx.doi.org/10.1080/10426509708545581>

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

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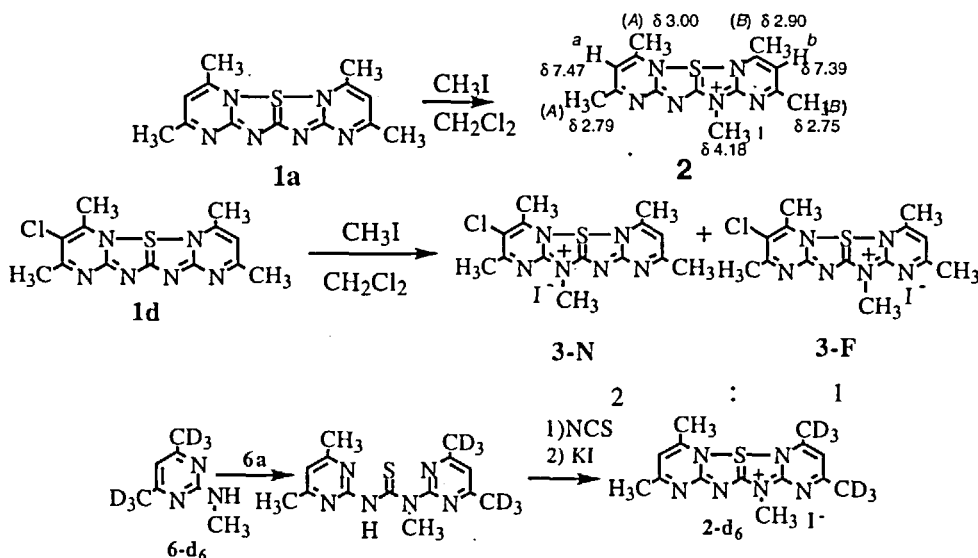
Selectivity of alkylation of and that of deuteration of methyl groups attached to the pyrimidine ring of tetraazathiapentalenes are discussed.

INTRODUCTION

Tetraazathiapentalenes **1** fused with pyrimidine rings are analogues 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 ability of the two nitrogens induced by the substituent at the pyrimidine ring.

RESULTS AND DISCUSSION

Methylation of symmetric **1a** afforded **2** exclusively. Methylation of 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.



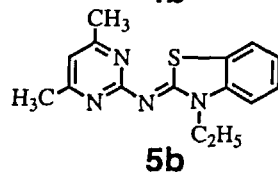
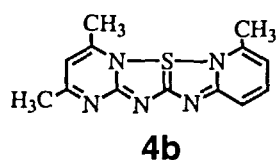
The deuteration of the methyl groups attached to the pyrimidine ring of **1** and **2** and related compounds were carried out ^1H NMR spectroscopically in CD_3OD solution at 80 °C under pseudo-first-order conditions. The kinetic study was carried out at the same concentration (1.36×10^{-2} mol/L) until 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 result from the very much faster position-exchange (rotation: 10^{-2} s^{-1}) of the methyl groups relative to the isotope exchange ($k = 10^{-4} - 10^{-5} \text{ s}^{-1}$).

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 pyrimidine ring of the B,B'-side which is closer to the thiadiazolium site. This is consistent with the chemical shifts of the methyl groups in the ^1H NMR spectrum. As expectedly, the isotope 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 Hydrogens in **1a**, **2**, **4b**, and **5b**

compd	solvent ^a	$k_A, k_{A'}$ (s^{-1})	$k_B, k_{B'}$ (s^{-1})
1a	B	1.5×10^{-5}	
4b	B	1.7×10^{-6}	
2	A	2.4×10^{-5}	3.5×10^{-6}
2	B	4.3×10^{-4}	6.9×10^{-5}
5b	A	1.6×10^{-6}	
5b	B	1.5×10^{-6}	



^a Solvent: A; CD_3OD , B; $\text{CD}_3\text{OD}/\text{CDCl}_3$ (volume ratio is 1 : 1).

Conditions: at 80 °C in 1.36×10^{-2} mol/l solution
for each substance.

REFERENCES

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