SYNTHESIS OF UNSYMMETRICALLY SUBSTITUTED 1,3,4,6-TETRAAZA-6a-THIA(S^{IV})PENTALENES AND THEIR ALKYLATION[1]

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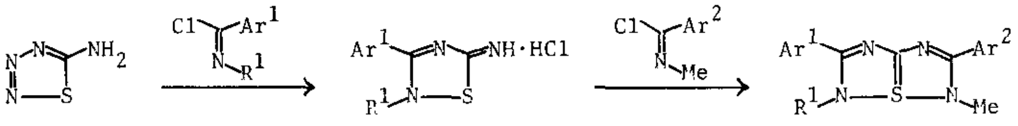
Abstract— Unsymmetrically substituted 1,3,4,6-tetraaza-6a-thia(S^{IV})pentalenes (1) with a methyl group at N(6) were prepared and alkylated with Meerwein reagents to give N(3) [or N(4)] mono-alkylated products, i.e., 1,3,4,6-tetraaza-6a-thia(S^{IV})pentalenium tetrafluoroborates (4).

We have reported recently on the presence of ring-transformation equilibrium effected by bond switch with participation of π-bonded S^{IV} in some thiathiophthene analogous systems.[1,2] In connection with this, it is of interest to investigate more closely whether the molecule of 1,3,4,6-tetraaza-6a-thia(S^{IV})pentalene is symmetric or unsymmetric in solution, and we prepared unsymmetrically substituted derivatives (1) which have a methyl group at N(6) according to the method reported by L'abbe' et al recently for the preparation of 1,2,5,6-tetraphenyl derivative.[3]

A typical example is as follows: N-methylbenzimidoyl chloride (9.0 ml, 60 mmol) was added to a suspension of 5-amino-1,2,3,4-thiatriazole (2: 6.13 g, 60 mmol) in dry acetonitrile (120 ml) and the resulting precipitates were filtered after nitrogen evolution had ceased. The precipitates were recrystallized from methanol to give 3a (11.5 g, 84%, mp 134-137 °C). To a solution of 3a (728 mg, 3.2 mmol) in dry pyridine (15 ml) was added N-methylbenzimidoyl chloride (0.5 ml, ca 3 mmol) with stirring under nitrogen at 0 °C and the mixture was heated at 100 °C for 3 h. Pyridine was evaporated under reduced pressure, and the residue was extracted with dichloromethane (30 ml x 2) after addition of water (50 ml). The residue after evaporation of the solvent was chromatographed (DCC, SiO_2) with dichloromethane-ether (4:1) to give 1a (755 mg, 77%, mp 197.0-198.5 °C) after recrystallization from benzene-hexane (1:1).

Yields and mp of **1** are shown in Table 1.

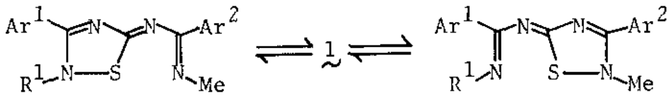


2 **3** **1** (1)

Table 1. Melting Points and Yields of Thiapentalenes (**1**)

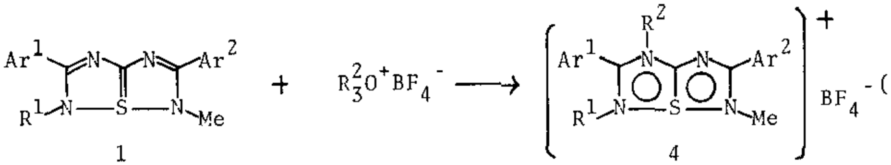
Compound	Ar^1	Ar^2	R^1	mp (°C)	Yield (%)
1a	Ph	Ph	Me	197.0-198.5	77
1b	Ph	Ph	p-MeC_6H_4	258.0-260.0	26
1c	Ph	Ph	p-$MeOC_6H_4$	252.0-253.5	25
1d	p-MeC_6H_4	Ph	Me	179.5-181.0	30
1e	Ph	p-MeC_6H_4	Me	179.5-181.0	51
1f	p-MeC_6H_4	p-MeC_6H_4	Me	243.5-244.5	52

Two unsymmetrical compounds, **1d** and **1e**, are identical and all compounds listed in Table 1 show only one N-methyl signal in NMR at 3.50 ± 0.02 (δ from TMS in $CDCl_3$) and NMR spectra of **1b** and **1e** showed no change at temperatures between 34 °C and -86 °C in CD_2Cl_2. This fact indicates that the molecule should be symmetric in nature or there is rapid valence isomerism in solution as shown in equation (2).

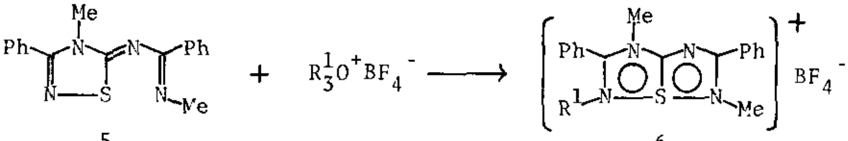


1' **1''** (2)

Then, **1** was alkylated with Meerwein reagents to see which atom is attacked among three possibilities, i.e., N(1), N(3), and S(6a). Alkylation was shown to take place at N(3) [or N(4)] and not at N(1) [or N(6)] and chemical shifts of all substituents were determined by comparison of the corresponding products of reactions (3) and (4). Results are shown in Table 2.



1 **4** (3)



5 6 (4)

Table 2. NMR Spectra of 1,3,4,6-Tetraaza-6a-thia(S^{IV})pentalenium Salts (4)*

Compound	Ar^1	Ar^2	$N(1)(R^1)$	$N(3)(R^2)$	N(6)(Me)	mp (°C)	Yield(%)
4a	Ph	Ph	Me, 3.38	Me, 3.72	Me, 3.86	223.0-224.0	88
4b	p-MeC_6H_4	p-MeC_6H_4	Me, 3.37	Me, 3.73	Me, 3.82	216.0-218.0	79
4c	Ph	Ph	Me, 3.36	Et, 4.25**	Me, 3.86	165.0-166.0	68
4d	p-MeC_6H_4	p-MeC_6H_4	Me, 3.32	Et, 4.25**	Me, 3.82	209.0-210.0	66
4e	Ph	Ph	Et, 3.67**	Me, 3.72	Me, 3.83	175.0-176.0	53

* δ from TMS in DMSO-d_6

** Chemical shift of the methylene quartet, that of the corresponding methyl triplet being at δ 1.33 ± o.ol with J=8 Hz.

A typical example is shown: A suspension of 1a (54 mg, 0.174 mmol) and trimethyloxonium tetrafluoroborate (128 mg, 0.87 mmol) in dry dichloromethane (10 ml) was stirred for 2 h at room temperature. TLC of the reaction mixture showed the absence of 1a. After addition of excess methanol, the mixture was evaporated and the residue was recrystallized from methanol-ether to give 61 mg (88%) of 1,3,6-trimethyl-2,5-diphenyl-1,3,4,6-tetraaza-6a-thia(S^{IV})pentalenium tetrafluoroborate (4a).

Indeed, identical product with 4a was obtained by the alkylation of 5 with triemthyloxonium tetrafluoroborate and the product of the same reaction with triethyloxonium tetrafluoroborate was different from 4c and identical with 4e, thus establishing the position of alkylation unambiguously. The structure of the alkylation product of a derivative of 5 where two phenyl groups are replaced by methyls has been determined by X-ray analysis and it was shown that the molecule is a planar 1,3,4,6-tetraaza-6a-thia(S^{IV})pentalenium tetrafluoroborate with N(1)——S and S—N(6) bond lengths of 1.984 and 1.833 A, respectively.[4] Hence, this reasult is another example of bond switch by alkylation, if it can be assumed that 1 is almost symmetric in solid state.

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References and Note

1. Part 10 of Chemistry of Hypervalent Sulfur, For Part 9, see: K. Akiba, T. Kobayashi, and S. Arai, *J. Am. Chem. Soc.*, **101**, 5857 (1979).
2. K. Akiba, S. Arai, T. Tsuchiya, and F. Iwasaki, *Angew. Chem. Int. Ed. Engl.*, **18**, 166 (1979) and references cited therein.
3. G. L'abbe', G. Verhelst, and G. Vermeulen, *ibid.*, **16**, 403 (1977).
4. K. Akiba, S. Arai, and F. Iwasaki, *Tetrahedron Lett.*, **1978**, 4117.
5. All **1** and **4a** gave correct elemental analyses. It is very difficult to obtain correct elemental analyses for **4** and results for other **4** are still to be examined.

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