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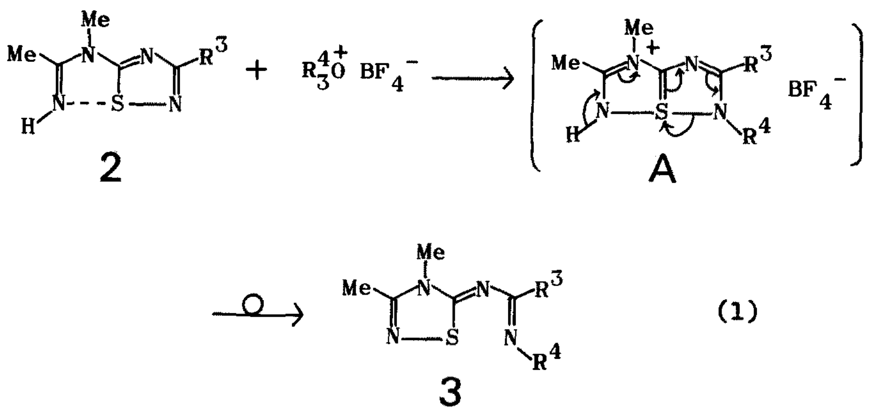
BOND SWITCH AT π-HYPERVALENT SULFUR IN THE ALKYLATION OF 1:1 ADDUCT OF 5-IMINO-Δ^2-1,2,4-THIADIAZOLINES WITH NITRILES 1)

Kin-ya Akiba* and Shin-ichi Arai
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan
Fujiko Iwasaki
Department of Material Science, The University of
Electro-Communication, Chofu-shi, Tokyo 182, Japan

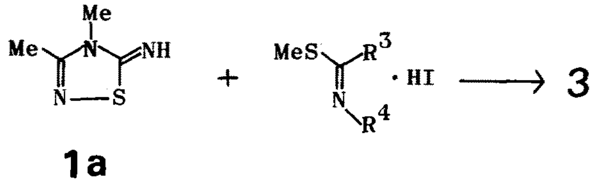
According to the finding that bond switch took place at π-hypervalent sulfur during the formation of 1:1 adduct (2) of 5-imino-Δ^2-1,2,4-thiadiazolines (1) with nitriles, we tried acylation and alkylation of 2 expecting to obtain further examples of bond switch. Here the successful results of alkylation are described, on the other hand, acylation was in vain, giving mere decomposition products.

The alkylation of 1:1 adduct (2) was carried out with Meerwein reagent in dichloromethane at ca. 40 °C, and the structure of the product was determined to be iminothiazoline derivative (3), which was supported by unequivocal synthesis via reaction (2). Yields and mp of 3 obtained by reaction (1) are as follows: 3: R^3, R^4, yield (%), mp (°C); 3a: Me, Me, 50, 121.5-122.5; 3b: Ph, Me, 33,2) 156.0-157.0; 3c: Ph, Et, 18,2) 103.0-105.0.
By reaction (2), 3 was obtained in a higher yield.

In reaction (1), alkylation took place at the nitrogen of position 2 of the thiadiazole ring and not at the expected imino nitrogen, thus the first bond switch by alkylation was exemplified.

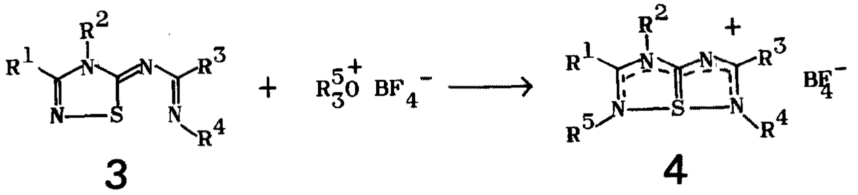


(1)



(2)

Further alkylation of 3 with Meerwein reagent was carried out in refluxing dichloromethane for ca. 1 hr to give 4 in a good yield.



(3)

Table Yield and mp of 4

	R^1	R^2	R^3	R^4	R^5	mp (°C)	Yield(%)
4a	Me^1	Me	Me^2	Me^2	Me^1	164.5–166.5	80
b	Me	Me	Me	Me	Et	127.5–129.5	78
c	Me	Me	Me	Et	Me	132.5–133.5	60
d	Me	Me	Ph^3	Me	Me	219.0–225.0	67
e	Me	Me	Ph	Me	Et	171.0–175.0	57

1) Me (R^1) of 4a, b and c appears at 2.57 and that of 4d and e at 2.63 ± 0.02 and Me (R^5) of 4a and c appears at 3.40 and that of 4d at 3.47 and long range coupling of the corresponding R^1 and R^5 was observed as braodening of the peaks compared to that of Me (R^3).

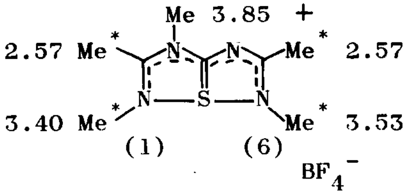
2) Me (R^3) of 4a, b, and c appears at 2.58 ± 0.01 and Me (R^4) of 4a and b at 3.53

and that of **4d** and **e** at 3.71 and long range coupling of the corresponding R^3 and R^4 was observed for **4a** and **b**.

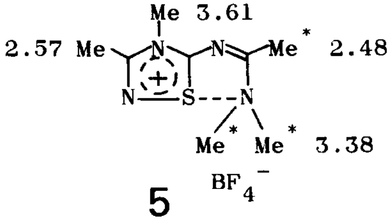
3) Phenyl (R^3) of **4d** and **e** appears as two multiplets at 7.5-7.8 (3H) and 7.8-8.1 (2H)[3].

That alkylation did not take place at the nitrogen with R^4, which is the most probably expected position, is apparent from the fact that two pairs of compounds, i.e., **4b** and **4c**, and **4d** and **4e**, are different each other and **4a** was different from **5**, which was prepared by another route.[4] Position of alkylation was definitely determined by comparison of NMR spectra of a series of five compounds, which is consistent with observation of broadening (by long range coupling) of two pairs of methyl peaks, i.e., Me (R^1) and Me (R^5), and Me (R^3) and Me (R^4). The phenyl of **4d** and **e** shows clearly separated two multiplets at 7.5-7.8 (3H) and 7.8-8.1 (2H) by which conjugation of the phenyl with the ring system is supported.[3]

Chemical shifts of five methyls of **4a** are shown with those of **5** (DMSO-d_6).



4a



5

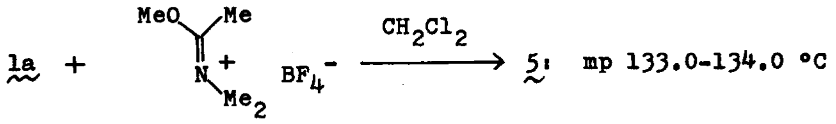
The exact structure of **4a** has been found to be 1,2,3,5,6-pentamethyl-1,3,4,6-tetraaza-6a-thia(S^{IV})pentalenium tetrafluoroborate by X-ray analysis of a single crystal.[5] Eight atoms of the ring are almost perfectly planar and bond lengths of N (1)——S and S——N (6) are 1.984 and 1.833 Å, respectively. Entire molecule of **4a** aquired better coplanarity than **2a** and bond length of N (1)——S decreased by 0.61 Å and that of S——N (6) increased by 0.17 Å from those of **2a**, indicating the presence of very strong interaction between the nitrogen and the sulfur. This fact can best be represented by π-sulfurane structure (**4a**) rather than **4a'**,[6] because the difference of the bond length of two S——N bonds (0.15 Å), caused by unsymmetrical nature of the molecule, is not too large for a thiathiophthene analog.[7)] Here again, apparent bond switch is observed by introduction of R^5.

From the results of this communication, partial aspect of importance and labile nature of π-sulfurane has been disclosed.

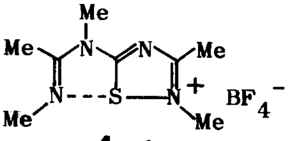
Acknowledgement: Authors are grateful to Itoh Science Foundation for partial support of this work.

References and Notes

1) Part 7 of Chemistry of Hypervalent Sulfur. For part 6, see: K. Akiba, T. Tsuchiya, N. Inamoto, K. Yamada, H. Tanaka, and H. Kawazura, Tetrahedron Lett., 1976, 3819.
2) Recovery of 2b was 31% in the preparation of 3b and 18% in that of 3c.
3) L. A. Lee and J. W. Wheeler, J. Org. Chem., 37, 348 (1972); R. N. Butler, Can. J. Chem., 51, 2315 (1973).
4) 5 was prepared by the following reaction in 76% yield:



5) F. Iwasaki and K. Akiba, To be published.
6) 2,3-Dimethyl-5-(1-methyliminoethylmethylamino)-1,2,4-thiadiazolium tetrafluoroborate (4a') can also fit the NMR data, but we describe the compound as π-sulfurane (4a) according to the reason in the text.



4a'

7) A. Hordvik and L. J. Saethre, Israel J. Chem., 10, 239 (1972). A. Hordvik and K. Julsham, Acta Chem. Scand., 26, 343 (1972).
8) 1:1 Adduct (2) was prepared by heating 5-imino-3,4-dimethyl-Δ^2-1,2,4-thiadiazoline (1) with excess imidate at 60-80 °C for several hours without solvent. The residue, after evaporation of excess imidate under reduced pressure, was recrystallized from benzene-hexane or benzene (40-80%).
9) All new compounds, 3, 4, and 5, gave correct elemental analyses and reasonble spectral data.

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