Tetrahedron Letters,Vol.24,No.44,pp 4859-4862,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

DECELERATED METHYL TRANSFER FROM σ-AMMONIOMETHYLSULFURANE COMPARED WITH THE CORRESPONDING METHYLSULFONIUM SALTS

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Abstract : The rate of methyl transfer to pyridine-d_5 of σ-ammoniomethylsulfurane, i.e., S, N-dimethyl-6, 7-dihydro-5H-dibenzo [b, g][1, 5] thiazocinium salt (**1**), was slower by 1300 times than that of methyldiphenylsulfonium salt (**3**). Activation parameters at 25 °C were obtained for **1**, ΔH^{*}=23.1, ΔS^{*}=-7.8, and for **3**, ΔH^{*}=18.1 kcal/mol, ΔS^{*}=-10.3 e.u., which are in accord with the hypervalent bonding of **1**.

Recently we have been challenging the synthesis of hitherto unknown alkylsulfuranes and prepared such a model as S, N-dimethyl-6, 7-dihydro-5H-dibenzo [b, g][1, 5] thiazocinium hexafluorophosphate (**1** : mp 195 - 197 °C). By examining ^{1}H NMR spectra, we concluded that **1** is σ-ammoniomethylsulfurane and determined the molecular structure by X-ray crystallographic analysis as shown in Fig. 1.$^{1)}$ The distance between the sulfur and the nitrogen is 2.446 Å and that of the methyl from the sulfur is 1.804 Å, and the methyl, sulfur, and nitrogen lie in almost a straight line ($\angle CH_3$-S-N= 176.9°), and the angle between the S — N bond and the $C_{eq}SC_{eq}$ plane is 74.0°. Thus the geometry around the sulfur is essentially a trigonal bipyramid, and therefore **1** was concluded as the first example of the stable σ-sulfurane with an apical methyl group.

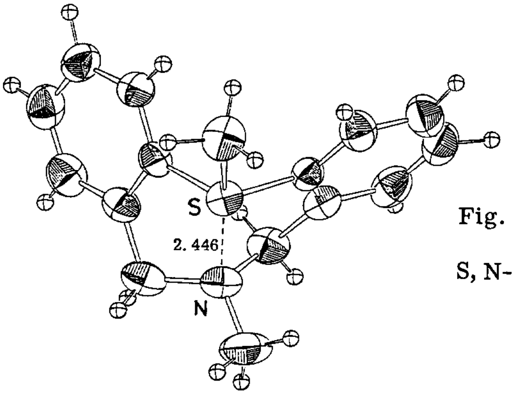
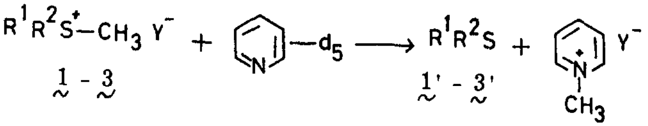


Fig. 1 ORTEP Drawing$^{2)}$ of S, N-Dimethylammonioalkylsulfurane (**1**)

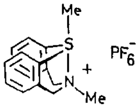
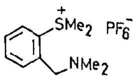
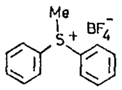
Since CH_3— S — N bond is apical bond and can be considered as three-center four-electron bond, the methyl group should bear less positive charge than those of ordinary sulfonium salts due to electron transfer from the nitrogen. Hence it can be expected that the rate of methyl transfer of 1 to a nucleophile should be slower than that of ordinary sulfonium salts.

On this standpoint, rates of methyl transfer to pyridine-d_5 from 1, dimethyl(o-dimethylaminomethyl)phenylsulfonium hexafluorophosphate (2),[3] and methyldiphenylsulfonium tetrafluoroborate (3) were measured using pyridine-d_5 as the solvent. Pseudo-first-order rate plots of concentration of the sulfonium salt as measured by the integral of the sulfonio methyl and that of the resulting sulfide as measured by that of the amino methyl (or pyridinio methyl) showed a very good straight line up to three half lives of the reaction (1). Apparent activation parameters were calculated according to Arrhenius equation.[4]



(1)

Table Rate Constants and Kinetic Parameters of Methyl Transfer

Compound	Temp (°C)	k_{obs}* (sec^{-1})	$\Delta H^{\ddagger}$ (kcal/mol) (25°C)	$\Delta S^{\ddagger}$ (eu) (25°C)	krel (25°C)
1 	45.0 35.0 25.0	1.82×10^{-5} 4.67×10^{-6} 1.48×10^{-6}	23.1	-7.82	1.0
2 	35.0 25.0 15.0	9.55×10^{-5} 3.54×10^{-5} 1.10×10^{-5}	18.5	-16.7	2.4×10
3 	35.0 25.0 13.8	5.25×10^{-3} 1.90×10^{-3} 5.60×10^{-4}	18.1	-10.3	1.3×10^3

The sum of the integrals of the sulfonio methyl of 1 and the ammonio methyl of 1' was taken as 100% and each concentration was calculated from relative intensity and the initial concentration of 1 (0.1 - 0.4 M). The initial concentration of 1 was calculated by the charged weight of 1 and pyridine-d_5 in an NMR tube.[4] Similar method was used for 2 and 3.

* Average value of duplicate runs (< ± 1%), temperature was controlled within ± 0.1 °C range.

Characteristic features in the Table are as follows :

i) The rate of methyl transfer of 1 is slower than that of 3 by thirteen hundred times.

ii) The activation enthalpy of the reaction of 1 is larger than that of 3 by five kcal/mol and the relative rate is mostly controlled by enthalpy of the reaction, although, on the other hand, activation entropy of the reaction of 1 is somewhat less negative than that of 3.

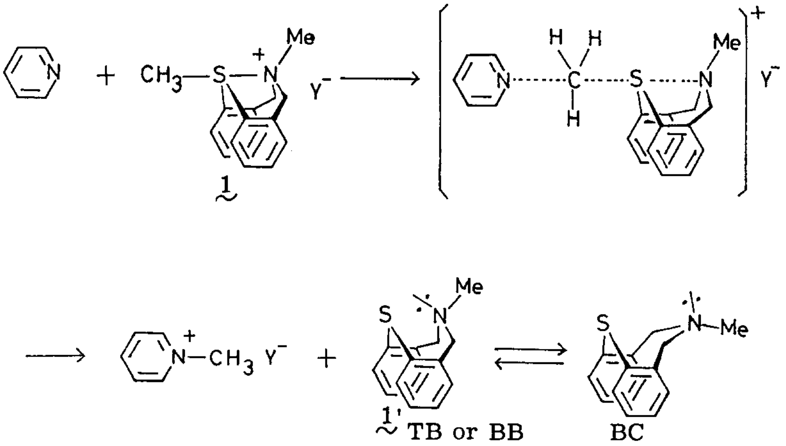
iii) The reaction rate of 2 is not so decelerated as expected, if there is N — S interaction as that in 1.[4c)] There is no evidence for direct interaction between the sulfonio group and the amino group as checked by ^{1}H NMR.[5)]

All these facts are compatible with the nature of three-center four-electron bond and molecular structure of 1 :

i) The larger activation enthalpy required for nucleophilic attack by lone pair of pyridine is the reflection of less positive charge on the sulfonio methyl group.

ii) Steric constraint around the nitrogen caused by S — N bond formation will be released at the transition state mainly due to elongation of the S — N bond, which is also broken in the product together with the C — S bond. This seems to be the origin of less negative value of activation entropy of 1 as compared with that of 3. Conformational analysis of the product has been investigated in detail and shown that boat-chair (BC) conformation is more stable and rigid than twist-boat (TB) and/or boat-boat (BB) conformations.[6)]

Now we have presented the first chemical evidence for unique character of σ-ammonioalkylsulfurane which is in accord with the nature of the hypervalent bond.



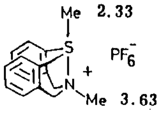
(2)

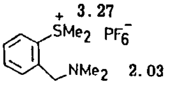
References and Notes

1) Detailed X-ray structural analysis will be published elsewhere : F. Iwasaki and K. Akiba et al. Summary of synthesis and structural study by ^{1}H NMR are reported in J. Am. Chem. Soc., **105**, 1983.

2) C. K. Johnson, ORTEP Report ORNL-3794, 1965, Oak Ridge National Laboratory, Tennessee, U. S. A.

3) Chemical shifts (δ from TMS in CD_3CN) of methyl groups are as follows :

1


2


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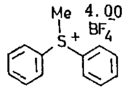
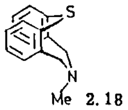
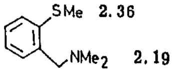
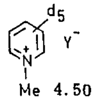


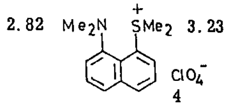
1'


2'


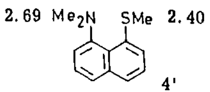


4) Kinetics of methyl transfer from methylsulfonium salts to amines has been well investigated to show that it obeys second-order rate law strictly. In the present case, it is difficult to evaluate the initial concentrations of the material exactly, therefore pseudo-first-order rates are shown in the Table. The value of 1.05 was used as the density of pyridine-d_5 (Stable Isotopes, Catalog No. 8, Merck Sharp & Dohme).
(a) E. D. Hughes and D. J. Whittingham, J. Chem. Soc., **1960**, 806.
(b) T. E. Young and A. R. Oyler, J. Org. Chem., **41**, 2753 (1976).
(c) J. K. Coward and W. D. Sweet, J. Org. Chem., **36**, 2337 (1971).
In the present reactions, the resulting sulfide (**1'** - **3'**) and methylpyridinium salt were observed quantitatively in NMR tubes and recovered in 70 - 100% yields after usual work-up.

5) Chemical shifts of amino methyls of **2** and **4** are close to those of the corresponding sulfides (**2'** and **4'**), which are in contrast to those of **1** and **1'**. This fact is attributed to steric hidrance due to congestion of four methyl groups.



4



4'

(in DMSO-d_6)

Y. Ohara, K. Akiba, and N. Inamoto, Bull. Chem. Soc. Jpn., **56**, 1508 (1983).

6) (a) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, J. Chem. Soc. Perkin I, **1976**, 913.
(b) L. E. Brieaddy, B. S. Hurlbert, and N. B. Mehta, J. Org. Chem., **46**, 1630 (1981).

7) New compounds (**1**, **2** and **2'**) gave satisfactory elemental analyses.

8) Partial support of this work was provided by a Grant-in-Aid for Scientific Research (No. 57430006) administered by the Ministry of Education, Science and Culture of Japanese Government.

(Received in Japan 23 July 1983)