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AN YLID EXCHANGE REACTION OF SULFILIMINE

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The reaction of new sulfilimine, N-2,4-dinitrophenyl-S,S-dimethylsulfilimine 1, with p-toluenesulfonamide gave N-p-toluenesulfonyl-S,S-dimethylsulfilimine 2. The reaction of 1 with carbon acids 3 having active methylene gave stable S-C ylids (exchange of S-N ylid for S-C ylid), while 2 reacted with malonitrile to give S-C ylid only in low yield. Thus, the ylid exchange mechanism based on the equilibrium including the protonated sulfonium salts has been assumed.

Recently, there have been much reported the studies of sulfilimines. These reports have been focused on N-sulfonyl and N-acylsulfilimines which are stable but lack the nucleophilicity.

Now a new type of sulfilimine 1, which seems to be more reactive than the sulfilimines mentioned above, has been prepared. Thus, 2,4-dinitrophenyl-S,S-dimethylsulfilimine 1 obtained in high yield from dimethylsulfoxide (DMSO) and 2,4-dinitroaniline[1] remained unchanged in N,N-dimethylformamide (DMF) at 100°C for 6 hr. and had also moderate reactivity as expected. In the present paper, we wish to describe an interesting ylid exchange reaction exhibited by this new S-N ylid.

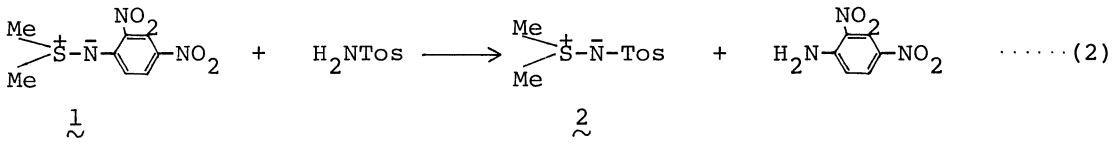
No ylid exchange reaction has been known, though the reaction (1) of sulfodiimide with amines giving other sulfodiimides has been reported[2].

$$RN{=}S{=}NR + H_2NR' \longrightarrow RN{=}S{=}NR' + H_2NR \quad \cdots\cdots (1)$$

At first, we examined the possibility of ylid exchange reaction of 1 for other sulfilimines.

After 4.0 mmol of 1 and 10 mmol of p-toluenesulfonamide were heated in DMF at 90°C for 7 hr., the solvent was removed by evaporation under reduced pressure. The resulting residue was column-chromatographed on silica gel with chloroform

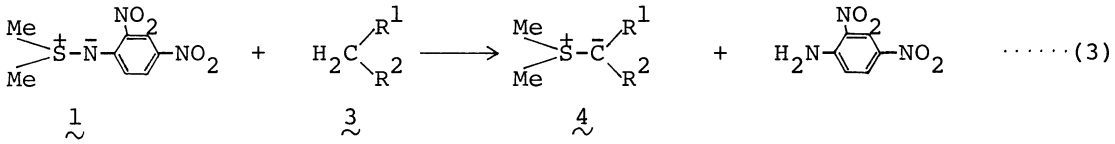
as eluent to give N-p-toluenesulfonyl-S,S-dimethylsulfilimine 2 in 58 % yield (mp. 154-155°C) and 2,4-dinitroaniline (2).



1 2 ·····(2)

In view of this fact, it is presumed that the possibility of ylid exchange is attributable to the more favorable delocalization of the negative charge on the nitrogen atom of the producing ylid, when the pKa value of the attacking agent, p-toluenesulfonamide (10.2), is smaller than that of leaving base, 2,4-dinitroaniline (15.8).

This result was expanded to other ylid exchange reactions of S-N for S-C (3). After 5.0 mmol of 1 and 10 mmol of carbon acid 3 (listed in Table 1) were heated in DMF at 90°C for 7 hr., the solvent was removed by evaporation in vacuum. The residue obtained was chromatographed on silica gel column with tetrahydrofuran as eluent to give sulfurane 4 and 2,4-dinitroaniline. The structure of 4 was decided comparing the melting point, IR, and NMR with authentic compound after recrystallization from tetrahydrofuran-n-hexane. The result is summarized in Table 1.



1 3 4 ·····(3)

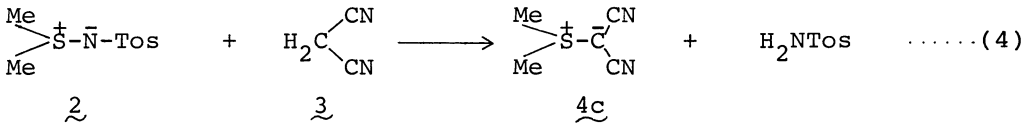
Table 1. Result of Reaction between 1 and 3.

	Carbon acid 3			Sulfurane 4	
	R^1	R^2	pKa	yield (%)	mp (°C)(lit.)
a	$COCH_3$	$COCH_3$	8.94[a]	94	167-8 (167-9)[3]
b	$COCH_3$	COC_2H_5	10.68[b]	80	63-5 (62-3)[3]
c	CN	CN	11.19[c]	98	100-1 (100-1)[4]
d	CO_2CH_3	CO_2CH_3		58	171-2 (169-70)[5]
e	$CO_2C_2H_5$	$CO_2C_2H_5$	13.3[d]	45	135-6 (134-5)[5]
f	C_6H_5	C_6H_5	34.1[e]	0	

a) G.Schwarzenbach and K.Lutz, Helv. Chem. Acta., 23, 1147 (1940).
b) M.L.Eidinoff, J. Amer. Chem. Soc., 67, 2072 (1945).
c) R.G.Pearson and R.L.Dillon, J. Amer. Chem. Soc., 75, 2439 (1953).
d) R.G.Pearson and J.M.Mills, J. Amer. Chem. Soc., 72, 1692 (1950).
e) A.Streitwieser,Jr., J.I.Brauman, J.H.Hammons, and A.H.Pudjaatmaka, J. Amer. Chem. Soc., 87, 384 (1965).

As shown in Table 1, it seems that the smaller the pKa of attacking group (carbon acid) is comparing with that of leaving group (2,4-dinitroaniline), the higher the yield of 4 is. In diphenylmethane with the larger pKa value than that of 2,4-dinitroaniline, sulfurane was not obtained.

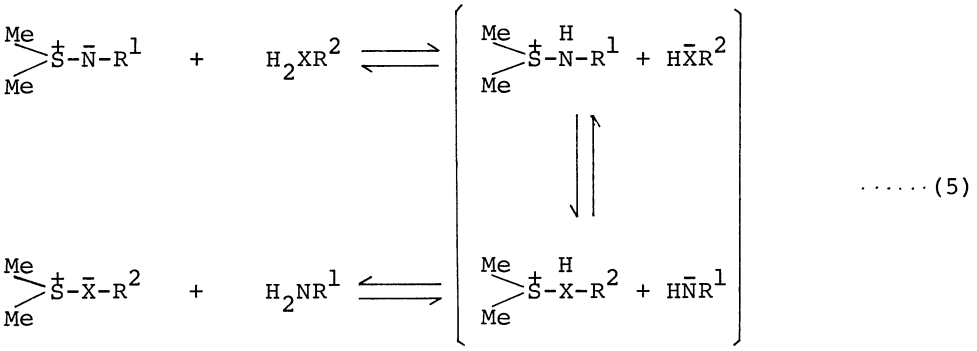
On the other hand, when N-p-toluenesulfonylsulfilimine 2 and malonitrile 3 were heated in DMF at 90°C for 7 hr., sulfurane 4c was obtained in 12.5 % yield.



2 3 4c ·····(4)

On the basis of the dependence on pKa value, the ylid exchange reaction was expected not to occur because the pKa value of the attacking carbon acid (11.19) is larger than that of the leaving sulfonamide (10.2). Nevertheless, the reaction gave the product corresponding to ylid exchange in low yield.

Therefore, it is presumed that the ylid exchange reaction may proceed in equilibrium reaction (5), and the equilibrium may incline toward the side in which the leaving group has a larger pKa value.



·····(5)

As an apparently analogous reaction of (5), there has been recently reported the reaction of imidodialkylsulfonium salt with amines (6).[6] However, these two types of reactions seem to be different in view of driving force of the reaction; higher stabilization of sulfonium cation in reaction (6), while higher stabilization of ylid anion in reaction (5).

Further works on the detail of this mechanism are in progress.

References

1) 1 was prepared by the modification of Claus' procedure (P.Claus and W.Vycudilik, Tetrahedron Lett., 1968, 3607). Thus, DMSO and 2,4-dinitroaniline were allowed to react in DMF at 0∼-10°C for one hr. using P_2O_5 as dehydrating agent. To the resulting solution, was added the three molar amounts of triethylamine to P_2O_5 to precipitate orange crystalline product (mp. 174°C (decomp.)) in 96 % yield. Reprecipitation from DMSO-MeOH afforded fine orange crystals of mp. 175-176°C (decomp.).

Found: C, 39.54; H, 3.81; N, 17.62; S, 13.49. Calcd. for $C_8H_9N_3O_4S$: C, 39.51 ; H, 3.73; N, 17.28; S, 13.18 %. IR: ν_{S-N}, 881; ν_{NO_2}, 1470, 1330 cm^{-1}. NMR (DMSO-d_6): δ 2.71 (1s, $S(CH_3)_2$), δ 6.90-8.20 (3d, aromatic).

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