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NOVEL REACTIONS OF AMINOOXOSULFONIUM YLIDE WITH EPOXIDES

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Reactions of (dimethylamino)phenyloxosulfonium methylide with epoxides were carried out. When aromatic epoxides were used as substrates, cyclopropyl sulfones and oxetanes were obtained. When aliphatic epoxides were used, the products were only the cyclopropyl sulfones. While the aminooxosulfonium ylide acts as a methylene transfer reagent to give the corresponding oxetanes, an intramolecular S_N2 type reaction of the betaines led to cyclopropyl sulfones.

Heteroatom-substituted oxosulfonium salts are interesting compounds. Johnson and coworkers have investigated the chemistry of aminooxosulfonium salts.1) We have reported the synthesis of diaminooxosulfonium salts and the reactions of these ylides with carbonyl compounds.2) Previously, we showed that the reaction of dimethyloxosulfonium methylide with epoxides (1) gave the corresponding oxetanes in good yields.3) Welch et al. also reported the synthesis of oxetanes by the reaction of methylphenyl(N-tosyl)sulfoximide anion with carbonyl compounds.4) As to the reactions of aminooxosulfonium ylide (2) with epoxides, we are interested in whether a similar methylene transfer reaction would occur to give oxetanes or another type of reaction would occur. In this paper, we report that the reactions of 2 with epoxides afford the corresponding cyclopropyl sulfones.

We first carried out the reaction of (dimethylamino)methylphenyloxosulfonium fluoroborate in the presence of bases. To a solution of 15 mmol of this salt in t-BuOH was added 15 mmol of t-BuONa in t-BuOH. After 30 min stirring, 10 mmol of 1,1-diphenyl-1,2-epoxyethane was added to this solution. After 2 days' refluxing, the reaction mixture was evaporated, washed with water, and extracted with hexane. A water- and hexane-insoluble solid was collected and dried to give 2,2-diphenylcyclopropyl phenyl sulfone (3a). The hexane extract was dried over $MgSO_4$ and evaporated. After work up, the crude product was chromatographed over Florisil to give 2,2-diphenyloxetane and N,N-dimethylbenzenesulfinamide. The results of reactions using different epoxides are shown in Table 1.

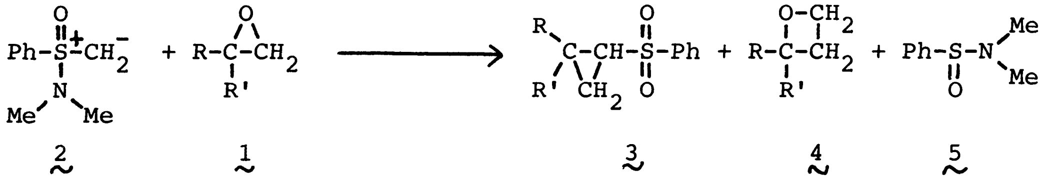
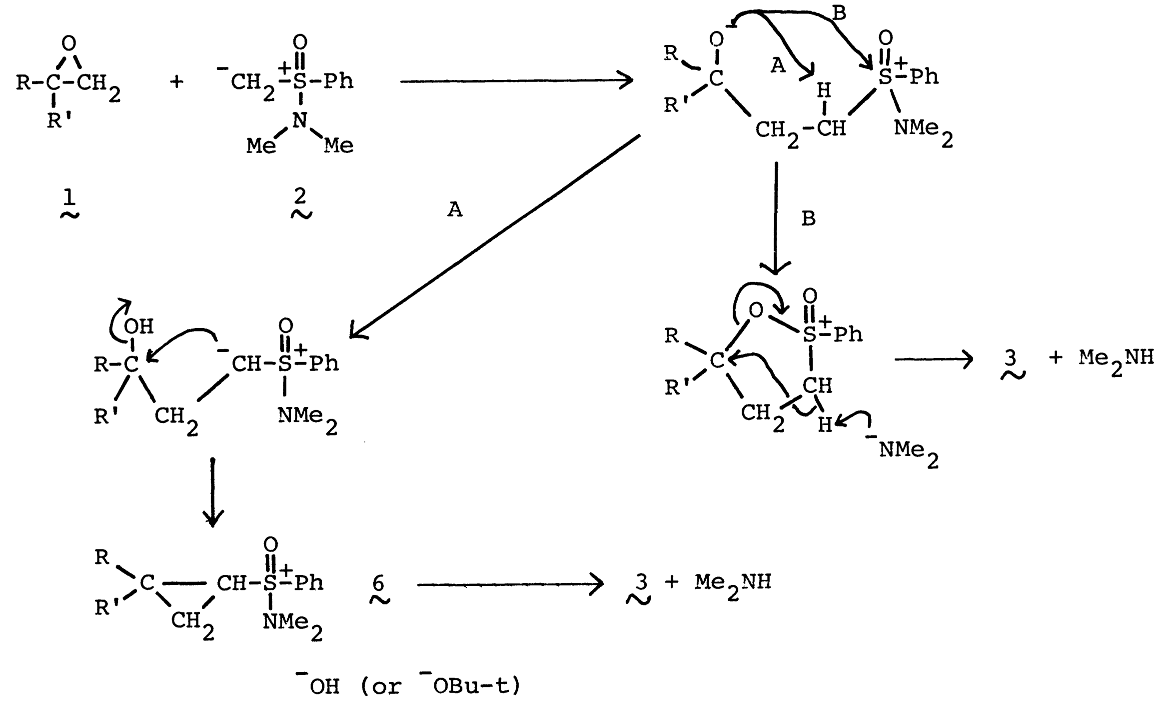


Table 1. Reactions of **2** with Epoxides.

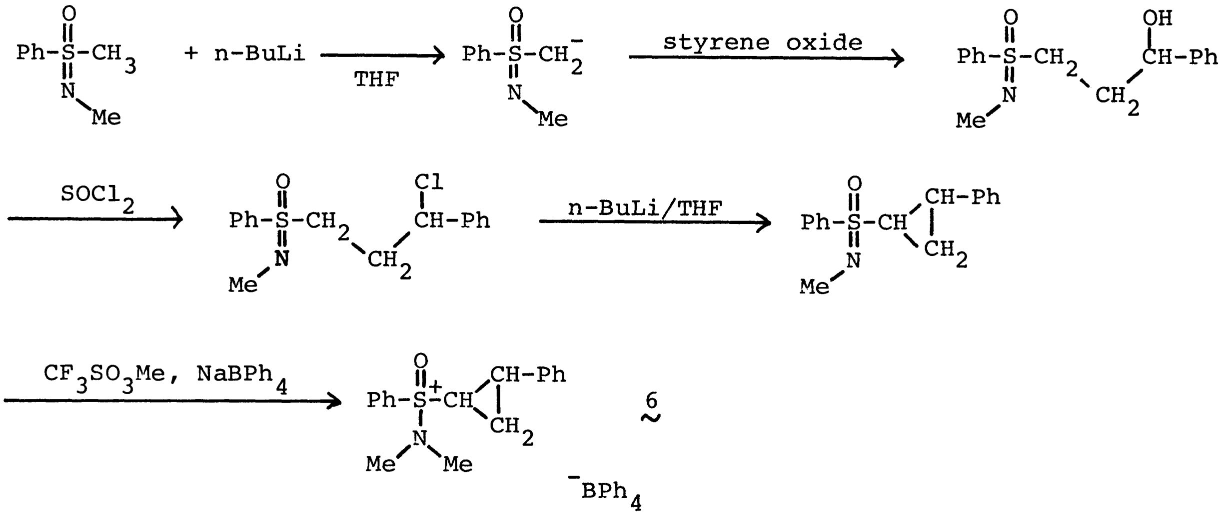
Epoxides[5]			Conditions	Excess ylide/%	Products[6] yield/%		
	R	R'			**3**	**4**	**5**
1a	Ph	Ph	t-BuONa, reflux, 2 d	50	42.0	31.0	54
1b	H	Ph	t-BuOK, reflux, 1 d	10	18.6	10.2	15[a]
1c	H	p-ClC_6H_4	t-BuOK, reflux, 6 h	10	10.9	5.5	10[a]
1d	Cyclohexylidene		t-BuONa, 50 °C, 2 d	15	45.0	0	0[a]
1e	4-Methyl-cyclohexylidene		t-BuONa, 50 °C, 2 d	50	64.6	0	0
1f	4-t-Butyl cyclohexylidene		t-BuONa, 50 °C, 2 d	50	68.0	0	0

a) Starting epoxides were recovered in yields of 20, 25, and 10% resp.

When epoxides with phenyl groups **1a**-**c** were used as substrates, both **3** and **4** were obtained in about 3:2 ratio. On the other hand, only **3** were produced in the cases of epoxides with cyclohexylidene groups (**1d**-**f**), which might be more reactive than aromatic epoxides. **4** might be formed by the methylene transfer reaction.[3] As to the formation of **3**, the following two are possible mechanisms.



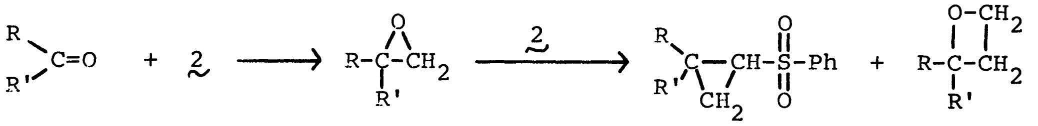
If A was the operative route, cyclopropylaminooxosulfonium salts 6 should be formed. To test this mechanism, 6 was prepared as follows.



6

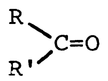
When 6 was allowed to react with t-BuOK/t-BuOH or NaOH/aq t-BuOH at 50 °C for two days, cyclopropyl sulfone 3b was not formed. This fact suggests that a correct route for 3 is not A but B. Thus, the ylide 2 attacks an epoxide to give the betaine in which the negatively charged O attacks the positively charged S, forming an unusual five-membered alkoxyoxosulfonium salt which is then converted to 3.

Since aminooxosulfonium ylides are used for the preparation of epoxides, we also carried out the reaction of 2 with carbonyl compounds. As shown in Table 2, a similar tendency was observed, but the yields of 3 and 4 were a little lower.



3 4

Table 2. Reactions of 2 with Carbonyl Compounds.[a]

Carbonyl compounds		Products yield/%[b]	
		3	4
7a	Benzophenone	35.0	23.0
7b	Benzaldehyde	16.0	8.0
7c	p-Chlorobenzaldehyde	15.0	7.6
7d	Cyclohexanone	42.0	0
7e	4-Methylcyclohexanone	56.0	0
7f	4-t-Butylcyclohexanone	59.0	0

a) Reactions were carried out at 50 °C for 2 days.

b) 50 mol% excess ylide was used.

In summary, reactions of **2** with epoxides gave the corresponding cyclopropyl sulfones via unusual five-membered cyclic alkoxyoxosulfonium ions. The reactivity of **2** with epoxides is quite different from that of dimethyloxosulfonium methylide.

We are now investigating the synthetic application of these reactions.

References

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6) Satisfactory values of elemental analysis were obtained for all new compounds.
7) **6**; mp 184-186 °C, ^{1}H NMR (CD_3SOCD_3) δ 1.65-1.93 (2H, m), 2.94 (6H, s), 3.14-3.16 (1H, m), 4.18-4.30 (1H, m), and 6.75-8.15 (30H, m).
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