The Mechanism of the Base Catalyzed Cleavage of Diphenyl Sulfide, Sulfone and Sulfonic Acid Ester[1]

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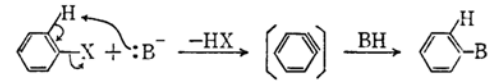
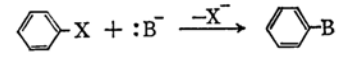
The cleavage reactions of diphenyl sulfide, sulfone and phenyl benzenesulfonate by strong bases have been known for many decades and studies on their product assay have been made by previous workers.[2] However, the mechanisms of these reactions have remained totally unclarified. Only recently the mechanism of the alkaline fusion of diphenyl sulfone has been rather extensively studied by the aid of ^{14}C and ^{18}O tracer techniques[3] and was suggested to involve the S_N2 type substitutions on both carbon and sulfur atoms.

Recently, Brotherton and Bunnett have demonstrated that diphenyl sulfone, sulfide and sodium benzenesulfonate react with sodium amide in boiling piperidine to give rise to *N*-phenylpiperidine and sulfinic acid or thiophenol in comparative yields.[4] They suggest that the reaction has proceeded by way of the initial attack of piperidide anion on the carbon atom bearing sulfonyl or sulfenyl group. In view of this particular reaction condition in which a very strong base is used, there remains a possibility that the reaction may proceed through the initial abstraction of *o*-hydrogen followed by the elimination of sulfone or sulfide group to form "benzyne" intermediate, to which piperidine adds to result the final product. Another possibility is that the reaction may proceed *via* the initial attack of the base on the sulfur atom as in the case of the alkaline fusion of diphenyl sulfone. These possible mechanisms are schematically illustrated as shown below.

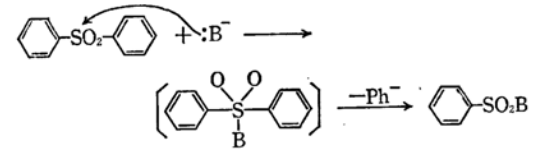
1) Benzyne Mechanism



2) S_N2 Substitution on Carbon



3) S_N2 Substitution on Sulfur



X=$-SO_2Ar$, $-SAr$; : B=a base

This paper will describe the detailed account of the mechanisms of the base cleavage reaction of diphenyl sulfide, sulfone and phenyl benzenesulfonate together with the corresponding *p*-methyl derivatives.

Results and Discussion

The reactants, bases used and the products obtained are shown in Table 1. The reactions were usually carried out in boiling piperidine in the presence of sodium amide or in hot DMSO containing potassium *t*-butoxide. The products were then carefully isolated by conventional distillation and recrystallization and identified by comparing their bp, mp, gas chromatograms and infrared absorption spectra with those of the authentic samples.

The results are summarized in Table 1.

Diphenyl Sulfide and Sulfone. Products isolated from the reaction of diphenyl sulfide were *N*-phenylpiperidine (I), thiophenol and diphenyl disulfide, while the reaction of diphenyl sulfone

1) Phenol and Phenolic Esters. XV.
2) W. E. Truce, D. P. Tate and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960); R. Otto, *Ber.*, **19**, 2425 (1886); C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, **1930**, 708; S. Oae and R. Kiritani, This Bulletin, **38**, 765 (1965); T. J. Broxton, Y. C. Mac, A. J. Parker and M. Ruane, *Aust. J. Chem.*, **19**, 521 (1966).
3) D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251; S. Oae and N. Furukawa, This Bulletin, **39**, 2260 (1966).
4) T. K. Brotherton and J. F. Bunnett, *Chem. & Ind.*, **1957**, 80.

Table 1. Experimental conditions and products

Substrate	Reagent	Products (yields in %)	Recovered (%)
$C_6H_5SC_6H_5$	$NaNH_2$-$C_5H_{10}NH$	C_6H_5SH(54%), $C_6H_5NC_5H_{10}$(74%), $(C_6H_5)_2S_2$(trace)	12%
$C_6H_5SO_2C_6H_5$	$NaNH_2$-$C_5H_{10}NH$	$C_6H_5SO_2H$(17%), $C_6H_5NC_5H_{10}$(29%)	16%
(p-MeC_6H_4)$_2S$	$NaNH_2$-$C_5H_{10}NH$	p-MeC_6H_4SH(51%), p-$MeC_6H_4NC_5H_{10}$(37%)	29%
(p-MeC_6H_4)$_2SO_2$	$NaNH_2$-$C_5H_{10}NH$	p-$MeC_6H_4SO_2H$(12%), p-$MeC_6H_4NC_5H_{10}$(73%)	7%
$C_6H_5SO_3C_6H_5$	$NaNH_2$-$C_5H_{10}NH$	C_6H_5OH(76%), $C_6H_5SO_2NH_2$(17%), $C_6H_5NC5H_{10}$(13%)	—
$C_6H_5SO_3C_6H_4Me$-p	$NaNH_2$-$C_5H_{10}NH$	p-MeC_6H_4OH(85%), $C_6H_5SO_2NH_2$(39%), p-$MrC_6H_4NC_5H_{10}$(10%)	—
$C_6H_5SC_6H_5$	t-BuOK-DMSO	t-$BuOC_6H_5$	
$C_6H_5SO_2C_6H_5$	t-BuOK-DMSO	t-$BuOC_6H_5$	

gave *N*-phenylpiperidine (I) and benzenesulfinic acid. All these products are apparently formed by the initial attack on benzene carbon bearing sulfur atom (mechanism 2). In no case, we could detect the formation of any product which is formed by the initial attack of the amide ion on the sulfur atom (mechanism 3). In order to examine the other possible route (benzyne mechanism), di-(*p*-tolyl) sulfide and sulfone were subjected to the reaction, since the mechanism 1 would require the formation of both meta- and para-substituted *N*-tolylpiperidines. The identification of both meta- and para-*N*-tolylpiperidines can be readily done by the comparison of their characteristic infrared absorption bands (*m*-derivative 10.5 μ, 12.95 μ; *p*-derivative 12.32 μ)[5] and also gas chromatograms. When the reactions were actually performed, we obtained only the para-substituted compound and could not detect the presence of the meta-*N*-tolylpiperidine among the products. Now that the mechanism 1 is also eliminated, the best plausible route for these reactions is shown to be the one involving the aromatic S_N2 process (mechanism 2).

Phenyl Benzenesulfonate. The reaction of phenyl benzenesulfonate gave not only *N*-phenylpiperidine but also benzenesulfonyl amide and phenol. While *N*-phenylpiperidine is a product formed by the substitution at the aromatic carbon, the other two products are considered to form by the initial attack of amide ion on the sulfur atom. In this case, *N*-phenylpiperidine would be a product of aromatic S_N2 type reaction (mechanism 2), but there remains a route involving benzyne intermediate. In our case, however, *p*-cresyl benzenesulfonate gave only *p*-tolylpiperidine, suggesting that the reaction proceeds through the aromatic S_N2 reaction process (mechanism 2), similar to the nucleophilic substitution of *p*-nitrohalobenzenes.

The Reaction of *t*-Butoxide in DMSO. Potassium *t*-butoxide catalyzed reactions of diphenyl sulfide and sulfone gave several products among which were identified *t*-butyl phenyl ether and phenol and much of the starting sulfide and sulfone were recovered unchanged.

Problem of Attacking Sites of Nucleophilic Reagents. All the above results indicate that the base cleavage reactions of diphenyl sulfide and sulfone proceed through the initial attack of the base on aromatic carbon atom bearing the functional group, while with the sulfonate, the main route is the initial attack of base on sulfonyl sulfur along with a side reaction involving the attack on the aromatic carbon atom similar to the case of the sulfide and sulfone. The reason of the difference between these two passways can easily be explained on the basis of the relative stabilities of the leaving groups. The initial attack of the sulfur atom of the sulfide or sulfone would have to give rise to the unstable phenyl anion as the leaving group, whereas the initial attack on the aromatic carbon atom bearing the sulfone or sulfide group should give either sulfinate or thiophenolate ion which would be a good leaving group. Thus the substitution on carbon atom will be more facile. While, in the case of the sulfonate, no matter which atom the nucleophile would attack, the leaving group is a very good one, namely, stable phenoxide ion in the case of sulfur attack, and benzenesulfonate ion in the case of the aromatic carbon attack. Therefore, both the sulfur and the carbon attack are expected to be quite facile and in fact it was found to be the case.

Experimental

Reagents. Diphenyl sulfide, sulfone, phenyl benzene-sulfonate, di-*p*-tolylsulfide, sulfone, *p*-tolyl benzenesulfonate were prepared by the standard procedures. Sodium amide commercially available was washed with anhydrous *n*-hexane before use. Potassium *t*-butoxide was prepared from *t*-butanol and potassium. Commercial piperidine was dried with sodium, bp 105—106°C. DMSO was distilled and dried over molecular sieve conventionally as usual.

Reaction and Product Isolation. A typical example of the experiments is as follows.

Diphenyl Sulfide with Sodium Amide in Piperidine. Sodium amide (2 g) was refluxed in 8 m*l* of piperidine for 30 min. To this solution was added 3 g of diphenyl sulfide and then the mixture was refluxed for 6 hr. After cooling, the solution was quenched with ice water to decompose sodium amide. The

5) R. Huisgen and J. Sauer, *Chem. Ber.*, **91**, 1453 (1958).

aqueous solution was extracted with ether. The aqueous layer was acidified with concentrated hydrochloric acid and extracted again with ether. After evaporation of ether, thiophenol was obtained (0.964 g) (54%). The first ether layer was extracted with concentrated hydrochloric acid and the separated ether layer gave the unreacted sulfide. The aqueous acidic solution was made alkaline with aqueous sodium hydroxide and extracted with ether, from which 1.19 g of *N*-phenylpiperidine was obtained (74%). All the products isolated were identified by comparing those IR spectra and gas chromatograms with those of the authentic samples.

All other sulfides, sulfones and sulfonates were treated similarly to diphenyl sulfide.

Potassium *t*-Butoxide in DMSO with Diphenyl Sulfide. Diphenyl sulfide 1.0 g and potassium *t*-butoxide 1.5 g were dissolved into 10 m*l* of DMSO. The solution was sealed into a glass tube and heated for 3 hr at 150°C. After cooling, the sealed tube was broken and the products were detected by gas chromatograph. The products are summarized in Table 1.