

REACTION OF BENZYNE WITH DISULFIDES

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Although it is reported that benzyne "inserts" into P-P bond of tetraethyl-diphosphine to give o-phenylenebisdiethylphosphine¹, any fruitful attempt has not been made on other heteroatom-heteroatom fission by benzyne. We now wish to report a new type of fission of disulfides with benzyne.

0.5 g atom of sodium was dissolved in 450 ml of liquid ammonia² and, into the resultant dark-violet solution was added 0.2 mole of dimethyl disulfide over a period of 10-15 minutes. After the mixture was stirred for an additional 10-15 minutes, 0.2 mole of bromobenzene was added over a period of 10-15 minutes and the mixture was stirred for 12-15 hours at -35° or below. Reaction was quenched by addition of ammonium chloride and usual work up gave thioanisole, diphenyl sulfide, biphenyl and a small amount of unidentified products (one of which was presumably biphenylene) from neutral part, thiophenol from alkaline extract and aniline and diphenylamine from acid extract, respectively. Yield of the products from several disulfides is shown in the Table. Identifications of products were made on nmr and IR spectra and VPC with authentic samples; eg. PhSH, isolated and distilled (78-79°/30mmHg); nmr, (CCl₄, TMS) τ 6.80 singlet (one proton) and τ 2.96 (five protons); IR, 3020-2840, 2550 (sharp, strong), 1600, 1580, 1470, 1440, many absorptions at 1400-1000, 900, 740 cm⁻¹; VPC, PEG 6000, 3m and Silicon DC 550, 2m.

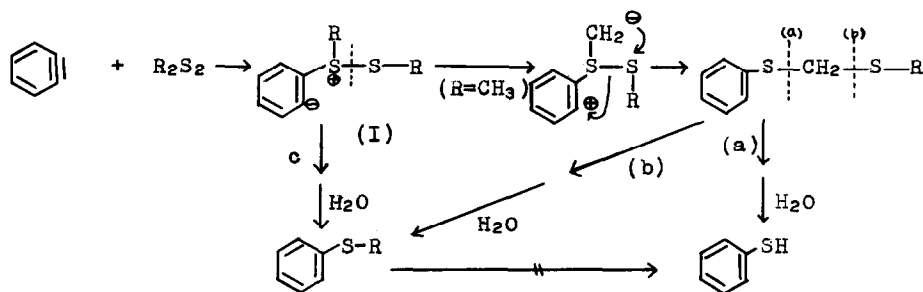
Thioanisole was obtained from distillation of neutral product (58-63°/6mmHg). IR absorption, 2900-3000, 1580, 1480, 1440, 1320, 1095, 1030, 970, 745, 690 cm⁻¹ and nmr spectrum; τ in CCl₄ 7.63 singlet (3 protons) and 2.97 (five protons). Its VPC (PEG 6000, 3m and Silicon DC 550, 2m) was identical with that of

authentic thioanisol.

Starting Disulfide R ₂ S ₂	Yield of Products (%)					
	PhSH	PhSR	Ph ₂ S	PhNH ₂	Ph ₂ NH	Ph ₂
R = CH ₃	{ 28	8	5	32	8	S ^{a)}
	{ 31	6	14	22	2.7	1
C ₂ H ₅	16	40	S	10	9	S
1-C ₃ H ₇	19	S	S	39	S	S
n-C ₄ H ₉	23	S	S	40	S	S
t-C ₄ H ₉	21	4	S	45	3	S
PhCH ₂	—	—	—	65	8	S
Na ₂ S	none	none	none	62	7	2

a) S; small amount

Although the mechanism of the reaction is not yet completely clear, the authors suggest that the following mechanism would be appropriate.



An alternative mechanism involving an intermediacy of sodium sulfide (expected cleaved product) is not operative, at least, in our condition because any thiophenol was not obtained in the reaction of benzyne and sodium sulfide (Table). Possibility of cleavage of thioether to thiophenol was also eliminated from the observation that thiophenol was not obtained from thioether in our condition.³ Reductive cleavage of C-S by sodium - ammonia is known and ylide formation from I is analogous to the reported reaction of benzyne with sulfide.⁴

References

- 1) F.A.Hart, J.Chem.Soc., 1960, 3324.
- 2) According to the procedure of R.Levine and C.R.Hauser, J.Am.Chem.Soc., 66, 1768 (1944).
- 3) Ascertained on phenyl ethyl sulfide. In the case of $t\text{-Bu}_2\text{S}_2$, ylide formation should not be operative and some of thiophenol could be formed through thioether.
- 4) V.Franzen H.Joschek and C.Mertz, Ann., 654, 82 (1962).