

REACTION OF BENZYNE WITH CARBON DISULFIDE

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We wish to report the hitherto unknown reaction of benzyne with carbon disulfide to give thioanisole, thiophenol and diphenyl sulfide.

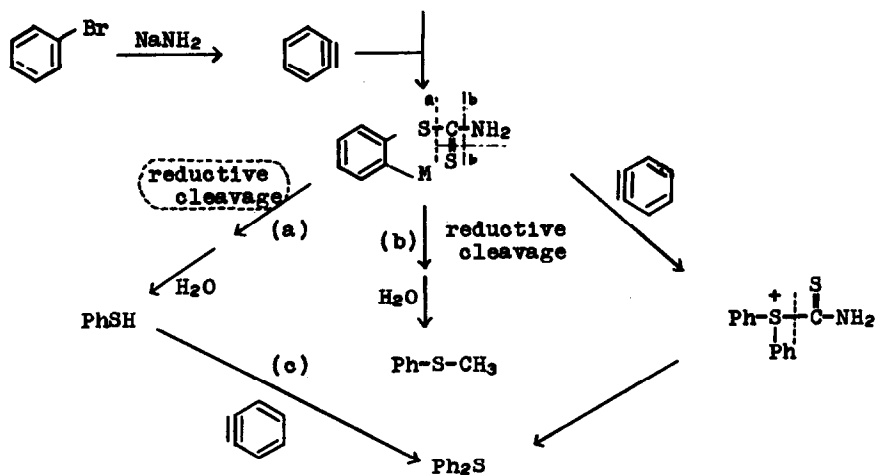
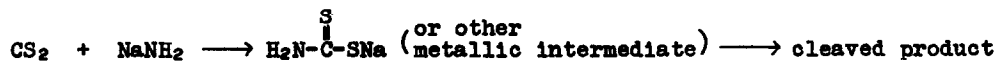
Metallic sodium and liquid ammonia were stirred for 1 hr and, into the resultant dark-violet solution was added an appropriate amount of carbon disulfide during 7 minutes. After ten minutes' stirring, bromobenzene was added into the solution and it was stirred for 14 hours. Usual work up gave acid fraction (A), amine fraction (B) and neutral fraction (N). (A) was practically pure thiophenol. b.p. 78-79°/30 mm Hg, nmr, (CCl₄, TMS) τ 6.80 singlet (one proton) and τ 2.96 (five protons); IR, 3020-2940, 2550 (sharp, strong), 1600, 1580, 1470, 1440 many absorptions at 1400-1000, 900, 740 cm⁻¹. Mixed VPC (PEG 6000, 3m and Silicon DC 550, 2m) with the authentic sample shows no peak-separation. (B) was consisted of aniline and diphenylamine. (N) was consisted of two products and on distillation (58-63°/6mm Hg) one of which was isolated and identified as thioanisole by means of IR 2900-3000, 1580, 1480, 1440, 1320, 1095, 1030, 970, 745, 690 cm⁻¹ and nmr spectra; in CCl₄, τ (TMS) 7.63 singlet (3 protons) and 2.97 (five protons); and VPC (PEG 6000, 3m and Silicon DC 550, 2m) with authentic sample. The other neutral product was identified as diphenyl sulfide. The total yield of the products was nearly quantitative (90% or more based on bromobenzene). Product composition was shown in the Table.

Table

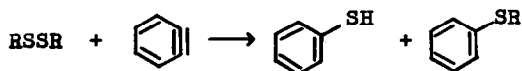
Expt. No	Reactant				Product Composition (mole %)				
	NH ₃ (ml)	Na (g)	CS ₂ (g)	Ph-Br (g)	PhSMe	PhSH	Ph ₂ S	PhNH ₂	Ph ₂ NH
1	600	22	31	31.4	18.7	19.4	8.3	48.2	5.4
2	250	5.5	6.1	6.3	16.9	18.2	12.2	41.8	10.9

If the carbon disulfide added more slowly, yield of thiophenol was increased in a sacrifice of thioanisole. Thus 25 minutes' addition of carbon disulfide in the same condition as Expt, No. 2 in the Table gave 23% yield of thiophenol and 11% yield of thioanisole.

Although the mechanism of this reaction is not yet decisively clear, the authors would present the following mechanism.



Reductive cleavage of C-S bond is a known reaction. In a similar manner, benzyne and dialkyl disulfides gave addition-cleavage products, thiophenol and alkyl phenyl sulfide, together with other products¹.



However, tetraethyldiphosphine was reported to add to benzyne, giving *o*-phenylenbisdiethylphosphine². Formation of diphenyl sulfide should not be limited to path (C) because thiophenol was obtained as a major product with a lesser amount of diphenyl sulfide in the reaction of benzyne with disulfides in the same reaction condition¹.

There has never been reported similar reaction of the type, so that our finding might afford a wide variety of application in the field of benzyne chemistry. Preliminary experiments showed that carbon dioxide instead of carbon disulfide gave phenol in our condition, where formation of benzoic acid was not observed. Absence of the latter in the product excluded the intermediacy of phenyl sodium or related metallic compound and formation of the former eliminated an alternative free radical mechanism from bromobenzene and metallic compound.

References

- 1) I. Tabushi, K.Okazaki and R.Oda, Tetrahedron Letters, in print.
- 2) F.A.Hart, J.Chem.Soc., 1960, 3324