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REACTIONS OF BENZYNE WITH CARBON DISULPHIDE IN THE GAS PHASE

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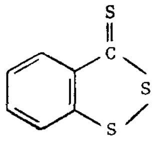
Benzyne in the liquid phase, generated from bromobenzene by elimination of HBr by sodamide in liquid ammonia, reacts with carbon disulphide to give thiophenol, thioanisole, diphenylsulphide, aniline, and diphenylamine.(1) In sharp contrast, benzyne in the gas phase, generated by elimination of CO_2 and CO from phthalic anhydride at 700°,(2) reacts with carbon disulphide to give none of the above mentioned products, but a 60% yield of material of molecular weight 184 instead.

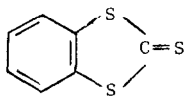
A solution of 1.48 g (0.01 mole) of phthalic anhydride in 9.06 ml (0.15 mole) of carbon disulphide was pumped into a Vycor tube filled with Vycor chips at 700° under nitrogen flowing at 10 cc per minute. Contact time was 23 seconds. The condensed effluent was extracted with 5% aqueous sodium hydroxide to remove 0.9 g (60%) unreacted phthalic anhydride and to recover 8.2 ml of carbon disulphide. The residue, 0.62 g, was analyzed by mass spectrometry (CEC model 21-103, 70 and 7.5 nominal ionizing volts, source and inlet at 250°), gas chromatography and directly-coupled gas chromatography-mass spectrometry.

The major product, by mass spectrometry, had the molecular weight 184 and an isotopic profile corresponding to three sulphur atoms, and thus the empirical formula $C_7H_4S_3$. Gas chromatography showed that dibenzothiophene, which also has the molecular weight 184, amounted to only 3.1% of the mixture which also contained 26.6% and 39% of two unknowns that eluted near each other and had close boiling points.

The two plausible isomers of formula $C_7H_4S_3$ that retain the ring intact are benzo-1,2-dithiol-3-thione (I) and benzo-1,3-dithiol-2-thione (II)



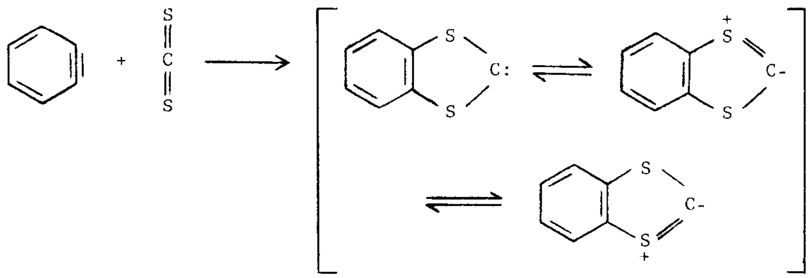
I



II

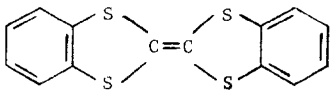
An authentic sample of I, kindly furnished by Professor R. Meyer of Dresden University, proved to have the identical retention time as the higher-boiling of the two unknowns (39%) in the gas chromatogram, as well as mass and nmr spectra identical to those of the eluted compound. II (26.6%), m.p. 164°, was isolated by trapping out, and the structure proven by elemental, mass-spectral, and nmr analyses.(3) Whereas the nmr spectrum of I is quite complex, as would be expected for protons on an unsymmetrically substituted benzene ring, II shows only a single peak in the aromatic region 7.42 ppm downfield from tetramethylsilane. Similar single peaks in the aromatic region have been observed for other symmetrically substituted benzenes such as *o*-xylene (Varian 201), catechol (Varian 124), and veratrole (Sadtler 1112).

I and II do not form by prior decomposition of carbon disulphide into S and CS; carbon disulphide alone under identical conditions as in its reaction with phthalic anhydride was recovered unchanged. Further, a separate reaction of sulphur with benzyne from phthalic anhydride at 700° gave four major products; benzotrithiole, thianthrene, benzothianthrene, and dibenzothiophene.(4) Of these, only dibenzothiophene and about half as much of thianthrene were found in the carbon disulphide reaction. The mode of formation of I and II may involve attack by a benzyne-CS_2 intermediate on another molecule of carbon disulphide to pluck off a sulphur atom, or formation of an adduct of benzyne with two molecules of carbon disulphide and loss of CS. The former mechanism would involve a 1,3-dipolar adduct such as III:



III

III is a carbenoid species and should give some dimer (IV):



IV (304)

By directly-coupled gas chromatography-mass spectrometry, product of molecular weight 304 and with the correct isotopic profile for four sulphur atoms was found at a level about 6% that of II.

4-Chlorophthalic anhydride and trimellitic anhydride react with carbon disulphide at 700° to give, in addition to I and II, the corresponding products retaining a chlorine atom and a carboxyl group, respectively. Our novel synthesis of benzodithiolthiones in one step from carbon disulfide and aromatic anhydrides thus appears to be general, and represents a distinct improvement over previous complicated and multi-step synthesis.

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References:

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