[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Reaction between Arsenicals and Di-(*p*-biphenyl)-thiocarbazone[1]

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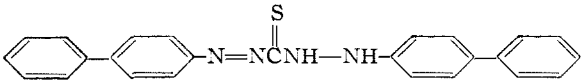
It has been noted[3] that diphenylthiocarbazones give a color change in the presence of small amounts of dichloroarsines. Di-(*p*-biphenyl)-thiocarbazone (DBT, I) has been studied in this connection,[3] and a considerable number of substituted diphenylthiocarbazones have been synthesized in this and other laboratories[4] for this purpose.



I

It was considered important to study more closely the nature of the reaction between arsenicals and DBT, since such a study might provide a basis for the use of thiocarbazones for quantitative determination of arsenicals, as well as give information of general chemical interest.

Preliminary attempts[5] to isolate the reaction product from DBT and an arsenical were unsuccessful, due to the instability of the material. In the present work, the reactions of DBT with ethyldichloroarsine, with arsenic trichloride and with arsenosobenzene (phenylarsine oxide) in benzene solution have been studied spectrophotometrically.

Experimental

Materials.—Merck reagent-grade **benzene**, which was used as the solvent throughout, was shaken with concentrated sulfuric acid and distilled. The DBT used was prepared at the University of Maryland, under the direction of Professor N. L. Drake, and melted at 170–170.5°. The **ethyldichloroarsine** used was redistilled twice, b. p. 69–70.5° (47 mm.).[6] **Arsenosobenzene**, prepared by the method of Blicke and Smith,[7] melted at 154–156°.

Measurements.—Absorption curves were measured with a Beckmann Spectrophotometer. No measurements were made on DBT solutions which were more than two days old; there was no detectable change in the extinction coefficient of DBT in solution over a period of thirty hours. Beer's law was assumed to hold for these solutions.[8]

Experimental Results

The absorption spectra of DBT, and of its reaction product with ethyldichloroarsine, arsenosobenzene and arsenic trichloride, were determined. DBT has a sharp maximum at 655 mμ, with a molar extinction coefficient of 57,000 and a second peak at 480 mμ. The reaction product of DBT and ethyldichloroarsine has a maximum at 510 mμ, the molar extinction coefficient being about 37,000. The product of reaction of DBT and arsenic trichloride showed maximum absorption at 460 mμ. The curves for DBT and its reaction product with arsenosobenzene are given in Fig. 1.

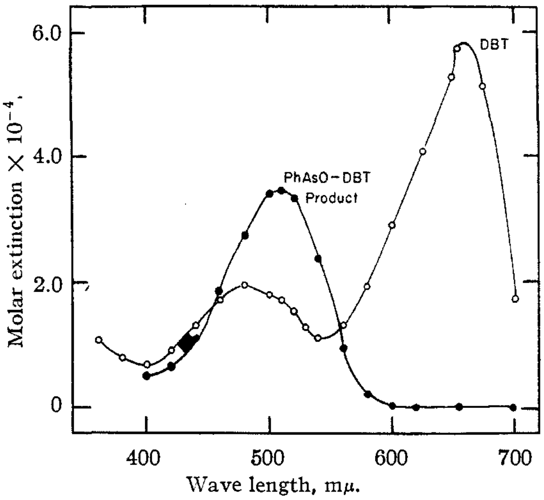


Fig. 1.

In the initial experiments, a constant amount of DBT and varying amounts of ethyldichloroarsine were mixed in 10 cc. of benzene, and the optical densities measured at 655 and 510 mμ. When the densities were plotted against the "reactant molar ratio" (moles arsenical/moles DBT) there was no break in the curves, the density at 655 mμ gradually decreasing with the increasing ratio of arsenical to DBT, and the density at 510 mμ gradually increasing.

The conclusion from these runs, that under these conditions the reaction had not gone to completion, was strengthened by the observation that in mixtures containing a large excess of arsenical exposed to the atmosphere and shaken, the reaction went rapidly to completion, changing from green to pink. Qualitative experiments showed that water, aniline or pyridine drove the reaction rapidly to completion, while dry air was without effect. In the next experiments, varying amounts of ethyldichloroarsine were added to

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[4] This work will be reported later.

[5] Experiments of Dr. Charles W. Todd in this Laboratory.

[6] Gibson and Johnson, *J. Chem. Soc.*, 2518 (1931), give 74.0° (50 mm.).

[7] Blicke and Smith, THIS JOURNAL, **51**, 3481 (1929); these authors report the melting point as 150°; lower values are given by earlier workers.

[8] Liebhafsky and Winslow, *ibid.*, **59**, 1966 (1937), showed that Beer's law was followed exactly by diphenylthiocarbazone in carbon tetrachloride. These authors noted that the thiocarbazone seemed to react with lead in glass containing lead oxide; in our work this did not seem to be a disturbing factor, although we used soft-glass pipets.

10 cc. of a 2.76×10^{-5} *m* solution of DBT containing one drop of pyridine. (Blank experiments showed that the addition of pyridine to a DBT solution of this concentration had no appreciable effect on the absorption curve.) The optical densities of the solutions at 655 and 510 mμ, when plotted against the reactant molar ratios, gave two curves, each of which consisted of a pair of straight lines intersecting at a molar ratio of 1.0 (Fig. 2.). This behavior showed clearly that under the conditions of the experiment one mole of DBT reacted with one mole of arsenical.

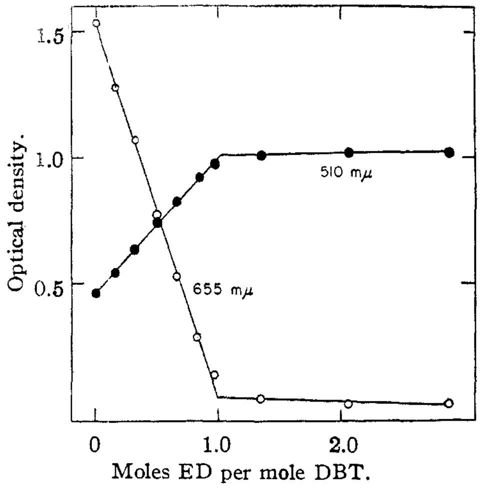


Fig. 2.

The reaction between DBT and arsenic trichloride was also investigated by the drop-of-pyridine technique; the curves obtained (Fig. 3) likewise show a molar ratio of arsenical trichloride to DBT of 1.0.

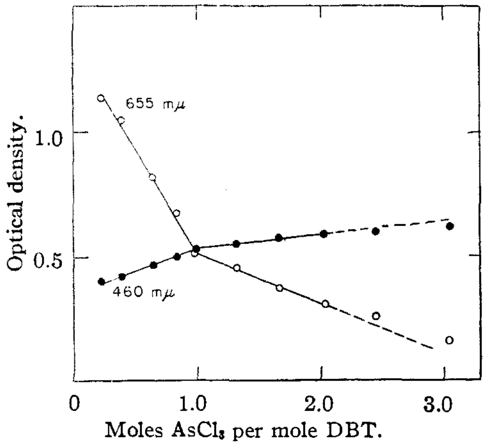


Fig. 3.

Since the dichloroarsines hydrolyze rapidly to the arsine oxides, it was considered important to determine whether an arsine oxide reacts with DBT in the same way as the dichloroarsines. For this purpose, arsenosobenzene and DBT were studied using the drop-of-pyridine technique. The pyridine was probably not necessary in this case to make the reaction go to completion, although this point was not investigated in detail. The results (Fig. 4) were the same as in the other two cases, showing a 1:1 molar ratio of the reactants. One significant difference between the reaction with arsenosobenzene and that with ethyldichloroarsine is that the latter is very fast, while the former requires several hours to reach completion, unless a considerable excess of the arsenical is present.

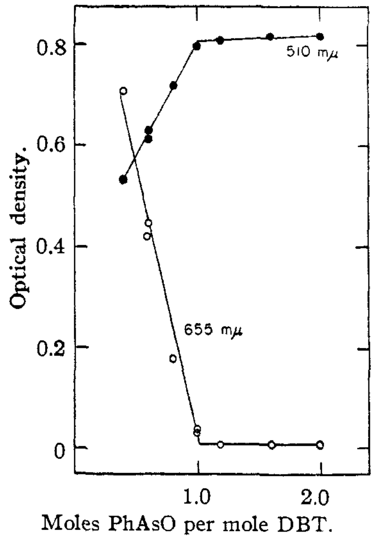


Fig. 4.

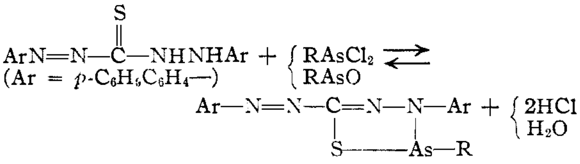
The following observations with arsenic trichloride support the idea that the reaction of DBT and arsenicals is an equilibrium process, which is driven to completion by the base. The absorption curve for a solution containing equimolar amounts of arsenic trichloride and DBT, and two drops of pyridine, showed a maximum at 460 mμ and a second lower one at 665 mμ. Then dry hydrogen chloride gas was passed through the solution, which caused a visible color change, and after centrifugation to clear up some turbidity, the absorption curve was redetermined. It was very similar in character to that of DBT, with a maximum at 480 mμ and a second one at about 665 mμ, the latter being much higher. These results are best explained on the basis that the hydrogen chloride reverses the reaction between arsenic trichloride and DBT, regenerating the latter.

The results obtained so far show that the reaction of DBT and the arsenical involves one molecule of each, in the presence of pyridine. In order to show that the reaction in the absence of pyridine (presumably under equilibrium conditions) involves one molecule of each, the reaction was studied by the method of continuous variations.[9] In determining the composition of the product of the reaction of A with B, a number of solutions are prepared in which the total concentration (A plus B) is constant. Some physical property (frequently optical density) of the various solutions is measured, and the differences (Y) between the values found and the values calculated, assuming no reaction had occurred, are obtained. The Y values are plotted against the "reactant mole fraction of A" (moles A/(moles A + moles B)), and the value of this function at which Y is *minimum* or *maximum* corresponds to the composition of the reaction product. If the maximum or minimum occurs at the same value of the reactant mole fraction of A for all of a number of wave lengths, only one equilibrium is present.

In applying this method to the reaction in question, eleven solutions were prepared in each of which the total concentration (ethyldichloroarsine plus DBT) was 6.60×10^{-5} *m*, and in which the reactant mole fraction of arsenical varied from 0.1 to 0.9; the optical densities of the solutions were measured at 620, 510 and 540 mμ. The curves (Fig. 5) all tend toward a maximum or minimum at a mole fraction of 0.5, indicating that the reaction in absence of pyridine involves one mole of each compound, and that (presumably) a second equilibrium is not present.

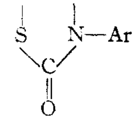
Discussion

The results above indicate that the reaction of arsenicals with DBT can be represented as follows



II

Structure II for the product has been suggested previously.[3] Compounds containing this ring system do not seem to have been described, but a series of compounds which are assigned structures of type III have been prepared by the action of dichlorides (phosgene, thionyl chloride, phthaloyl chloride, etc.) on diphenylthiocarbazone.[10]



III (from phosgene)

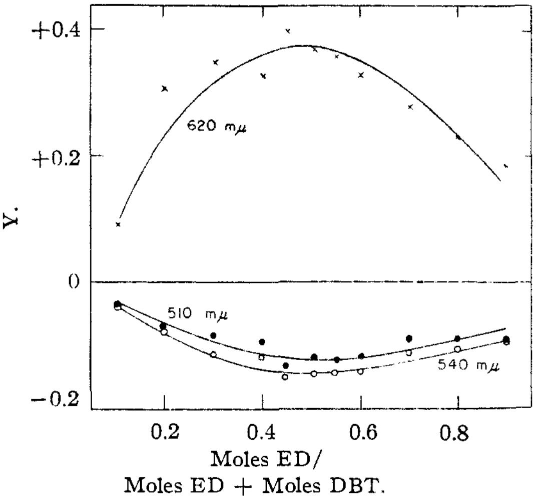
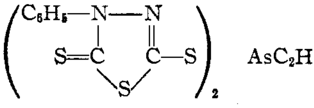


Fig. 5.

The other structure for the reaction product of an arsenical and DBT, which was considered likely before the present experiments were carried out, involved a combination of two molecules of DBT with one of arsenical. This structure was considered because of the well-known tendency to form arsenic–sulfur bonds, and because a compound of structure IV has been isolated from the action of ethyldichloroarsine on the appropriate thiol.[5] In this case, however, there is no opportunity for the formation of the 1:1 product.



IV

The effect of bases in displacing the equilibrium leading to II, with the dichloroarsines, is clear enough. The similar effect of water must be due to the removal of hydrogen chloride from the equilibrium by some mechanism such as solvation.

Summary

On the basis of a spectrophotometric study, it is concluded that the reaction of di-biphenylthiocarbazone with ethyldichloroarsine, with arsenosobenzene and with arsenic trichloride involves one mole of arsenical to one mole of the thiocarbazone. In the absence of base or of water, the reaction does not go to completion, and is probably an equilibrium reaction.

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[9] Job, *Ann. chim.*, [10] **9**, 115 (1928); Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941); Gould and Vosburgh, *ibid.*, **64**, 1630 (1942).

[10] Freund and co-workers, *Ber.*, **23**, 2821 (1890); **26**, 2494, 2869 (1893).