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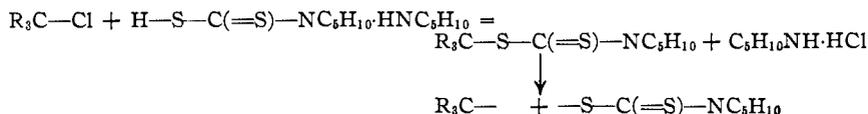
THE INTERACTION OF DIARYLARSYL IODIDES, DIARYLSTIBYL IODIDES AND PHENYLDIHALOARSINES WITH THE PIPERIDINE SALT OF N-PENTAMETHYLENE-DITHIOCARBAMIC ACID¹

BY F. F. BLICKE AND U. O. OAKDALE²

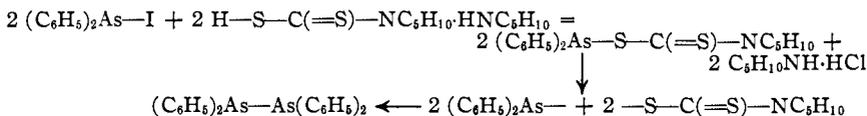
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N-Pentamethylene-S-triarylmethyldithiourethans are formed almost instantly and quantitatively from the interaction, at ordinary temperature, of a triarylmethyl halide and the piperidine salt of N-pentamethylenedithiocarbamic acid. These urethans are of interest because of the fact that they dissociate spontaneously, in solution, with the formation of triarylmethyls.³



In view of the great reactivity of the halogen in diarylarsyl and diarylstibyl iodides it seemed probable that these halides, too, might react with the piperidine salt of N-pentamethylenedithiocarbamic acid similarly to the triarylmethyl halides. It was found that piperidine hydriodide was precipitated almost immediately upon the addition of diphenylarsyl iodide, dissolved in benzene, to the piperidine salt of the dithiocarbamic acid. A colorless, crystalline compound was isolated from the benzene solution which, according to the results obtained from an analysis and molecular weight determination, was N-pentamethylene-S-diphenylarsyldithiourethan.



Di- α -naphthylarsyl iodide, biphenylenearsyl iodide, 6-iodophenoxarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted with the piperidine salt in a manner entirely analogous to that described.

In the event that N-pentamethylene-S-diphenylarsyldithiourethan behaved similarly to the triarylmethyl analogs it should yield spontaneously, in solution, diphenylarsyl which would then polymerize, partly or com-

¹ This paper represents the second part of a dissertation to be submitted to the Graduate School by Mr. Oakdale in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² Parke, Davis and Company Fellow.

³ Blicke, *THIS JOURNAL*, **45**, 544 (1923).

pletely, to tetraphenyldiarsyl. This compound, as well as other tetraaryldiarsyls, absorbs with great rapidity an amount of oxygen which corresponds to that required for the formation of a peroxide.⁴ Tetraphenyldiarsyl reacts with oxygen in a similar manner.⁵

In one series of experiments the reactivity of the dithiourethans toward oxygen was tested by the use of the original reaction mixture. A number of sealed tubes were prepared; each tube contained the iodide, the required amount of the piperidine salt of *N*-pentamethylenedithiocarbamic acid and bromobenzene. After twenty-four hours the tubes were broken in an absorption apparatus and the contents exposed to oxygen, with continuous agitation, for two hours. No absorption of oxygen was noticed in any instance. Absorption experiments were repeated with the isolated dithiourethans with negative results.

Phenyldichloro- and phenyldi-iodoarsine react readily with two molecular equivalents of the piperidine salt of the dithiocarbamic acid from phenylarsylene *N*-pentamethylenedithiocarbamate, $C_6H_5As[S-C(=S)-NC_6H_{10}]_2$. Other alkyl- and aryldihaloarsines would, undoubtedly, react in an analogous manner. Many alkyl- and aryldihaloarsines are liquids or low melting solids, hence, it is difficult if not impossible to identify small amounts of these substances. No entirely satisfactory derivatives have been described hitherto which can be used for identification purposes; the dithiocarbamate, however, which can be obtained in sufficient amount from one drop of either of the above mentioned halides, seems to be especially suitable for this purpose because of the ease of its preparation,⁶ the high molecular weight, sharp melting point and the low loss of material on recrystallization.

Experimental Part

***N*-Pentamethylene-S-diphenylarsyldithiourethan.**—Two hundredths of a mole of diphenylarsyl iodide, dissolved in the smallest possible amount of warm benzene, was added to 0.02 mole of the piperidine salt of *n*-pentamethylenedithiocarbamic acid,⁷ dissolved in warm benzene. Piperidine hydriodide precipitated immediately. The mixture was protected from moisture and after twelve hours the piperidine salt was removed by filtration and about 30 cc. of petroleum ether (30–60°) was added to the filtrate in order to precipitate a small quantity of piperidine hydriodide which had remained in solution. The hydriodide weighed 4.0 g.; the calculated amount is 4.2 g. To the benzene-petroleum ether solution there was added 150 cc. of petroleum ether whereupon the *N*-pentamethylene compound precipitated in crystalline form. The yield of the

⁴ Blicke and Smith, *THIS JOURNAL*, **51**, 2272 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930).

⁵ Blicke and Oakdale, *ibid.*, **53**, 1025 (1931).

⁶ In order to obtain the reagent it is merely necessary to add piperidine to a solution of carbon disulfide in absolute ether; the piperidine salt of the dithiourethan precipitates immediately.

⁷ Cahours, *Ann. chim. phys.*, [3] **38**, 88 (1853); Ladenburg and Roth, *Ber.*, **17**, 514 (1884).

latter was 5.2 g. It was washed thoroughly with water to remove traces of piperidine hydriodide, dried and recrystallized from acetic acid or ethyl acetate.

Neither the original reaction mixture⁸ nor the pure, isolated dithiourethan absorbed oxygen.

The molecular weight was determined in boiling benzene by the Menzies method. Calcd. mol. wt., 389; found, 386.

Dissolved in acetone the compound decolorized potassium permanganate, as well as iodine, instantly.

Diphenylchloroarsine was formed when the benzene solution of the compound was treated with hydrogen chloride at ordinary temperature.

A few drops of sulfuric acid were added to an acetic acid solution of the material and the mixture boiled for a few minutes. Diphenylarsinic acid was obtained as a reaction product.

Di- α -naphthylarsyl iodide, biphenylenearsyl iodide, 6-iodophenoarsine, diphenylstibyl iodide and di-*p*-tolylstibyl iodide reacted in a similar manner with the piperidine salt of the dithiocarbamic acid.

TABLE I
DITHIOURETHANS

Iodide used in preparation	M. p., °C.	Formulas	As, Sb or Bi, %		S, %	
			Calcd.	Found	Calcd.	Found
Diphenylarsyl	114-115	C ₁₈ H ₂₀ S ₂ NAs	19.26	19.42	16.47	16.61
Di- α -naphthylarsyl ^a	214-215	C ₂₆ H ₂₄ S ₂ NAs	15.33	14.99	13.11	12.57
Biphenylenearsyl ^b	155-158	C ₁₈ H ₁₈ S ₂ NAs	19.36	19.31	16.56	16.39
6-Iodophenoarsine ^b	105-106	C ₁₈ H ₁₈ OS ₂ NAs	18.59	18.50	15.90	15.51
Diphenylstibyl ^c	124-127	C ₁₈ H ₂₀ S ₂ Nsb	27.92	27.77	14.70	14.54
Di- <i>p</i> -tolylstibyl ^d	123-124	C ₂₀ H ₂₄ S ₂ Nsb	26.23	26.19	13.82	13.66

^a Blicke and Smith, *THIS JOURNAL*, **51**, 1565 (1929).

^b Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 781 (1930).

^c Blicke, Oakdale and Smith, *ibid.*, **53**, 1026 (1931).

^d The preparation of this iodide will be described in a later paper.

Phenylarsylene N-Pentamethylenedithiocarbamate, C₆H₅As[S—C(=S)—NC₂H₁₀]₂.—The following experiment illustrates the serviceability of the piperidine salt of the dithiocarbamic acid as a reagent for the identification of a very small quantity of phenyldi-iodoarsine. To one drop (0.0306 g.) of the latter compound there was added 0.127 g. (five times the calcd. amount), of the piperidine salt dissolved in about 3 cc. of dry benzene. The mixture was protected from moisture and after twelve hours the benzene was allowed to evaporate. The crystalline residue was washed with water until the piperidine hydriodide and excess piperidine salt of the dithiocarbamic acid had

⁸ As a control experiment the reaction mixture obtained from 1.61 g. (0.005 mole) of triphenylmethyl bromide and 0.005 mole of the piperidine salt of the dithiocarbamic acid, dissolved in bromobenzene, was placed in the absorption apparatus and shaken vigorously. Previously, absorption experiments in the case of N-pentamethylene-S-triarylmethyldithiourethans had been carried out only with the isolated urethan. After one hour the reaction mixture had absorbed 60 cc. of oxygen and after two and one-half hours over 100 cc. had been absorbed. An absorption in excess of 56 cc., the required amount of gas for peroxide formation, is to be expected because of the union of the sulfur radical, formed during the dissociation of the dithiourethan, with oxygen. The formation of sulfur dioxide, or other volatile product, during the absorption naturally render the absorption procedure only a semi-quantitative one. Two-tenths of a gram of pure triphenylmethyl peroxide was isolated from the mixture.

been removed completely. The crude product weighed 0.022 g. One-half of the material was recrystallized from ethyl acetate; m. p. 173–174°.

Phenyldichloroarsine reacts in an analogous manner.

Anal. Calcd. for $C_{18}H_{26}S_4N_2As$: As, 15.87; S, 27.15. Found: As, 15.76; S, 26.92.

Summary

Diarylarsyl and diarylstibyl iodides react readily with the piperidine salt of N-pentamethylenedithiocarbamic acid to form N-pentamethylene-S-diarylarsyl- and N-pentamethylene-S-diarylstibyl dithiourethans. Unlike the triarylmethyl analogs these substances do not undergo spontaneous decomposition in solution to form compounds of the type $R_2As-AsR_2$ and $R_2Sb-SbR_2$. Phenyldihaloarsines and the piperidine salt of the dithiourethan interact to yield a dithiocarbamate. Because of the advantageous properties of this substance the piperidine salt of the dithiocarbamic acid is suggested as a reagent for the identification of small quantities of alkyl- and aryl dihaloarsines.

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[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

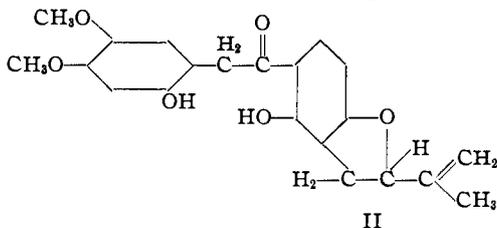
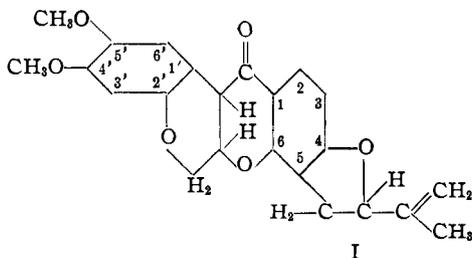
ROTENONE. XXII. SOME NEW DATA IN CONFIRMATION OF THE STRUCTURE OF ROTENONE

BY L. E. SMITH AND F. B. LAForge

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The complete formula for rotenone having been established on the basis of its principal reactions as I,¹ reference should be made to several other typical reactions not explained in previous articles.



¹ LaForge and Haller, *THIS JOURNAL*, **54**, 810 (1932).