yellow needles. After repeated recrystallization from petroleum ether containing a few drops of ether these melted at 89–90°.

Anal. Calcd. for $C_{14}H_9O_2Br$: C, 58.1; H, 3.1. Found: C, 58.9; H, 3.4.

p-Bromobenzil, XXI, is readily soluble in all organic solvents. It has a pronounced tendency to separate from solution as an oil and consequently is extremely difficult to purify. The analyses show that our sample was contaminated with benzil. Our melting point, therefore, is doubtless a little too low but the fact that the substance readily formed a quinoxaline derivative and was oxidized to equivalent quantities of benzoic and *p*-bromobenzoic acids by alkaline hydrogen peroxide leaves no doubt as to its character.

The Anhydro Compound, Ethylidene-α,β-diphenyl-β-bromobenzoyl-vinylamine, XX.—The anhydro compound was made like its bromine-free analog. It crystallizes from ether and from methyl alcohol in very pale yellow needles and melts at 102°.

Anal. Calcd. for $C_{23}H_{18}ONBr$: C, 68.3; H, 4.5. Found: C, 68.7; H, 4.7.

Ozonization.—The substance was ozonized in ethyl bromide. The products, isolated in the same manner as those from the bromine-free compound, were *p*-bromobenzil and benzamide.

Hydrolysis. α,β-Diphenyl-β-bromobenzoyl-vinylamine, XXVI.—Like its bromine-free analog, the anhydro compound is hydrolyzed with the utmost ease to acetaldehyde and a yellow, unsaturated amine. The amine was purified by recrystallization from acetone and methyl alcohol. It is readily soluble in acetone, moderately soluble in ether, sparingly soluble in methyl alcohol. It crystallizes in deep yellow needles and melts at 172°.

Anal. Calcd. for $C_{21}H_{16}ONBr$: C, 66.7; H, 4.2. Found: C, 67.4; H, 4.7.

Summary

This paper contains a description of the isolation of two pseudo bases in the triphenyl isoxazole series, an account of their properties, an opinion as to their structure, and a discussion of the mechanism by which such pseudo bases are formed from their salts.

Cambridge 38, Massachusetts

[Contribution from the Chemical Laboratory of the University of North Carolina]

PARA-CYMENE STUDIES. XI. PARA-CYMYL-2-CARBITHIOIC ACID

By Alvin S. Wheeler and Charles L. Thomas[1]

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Fleischer[2] was the first to make a dithio acid, the dithio-benzoic acid. Two years later Engelhardt, Latschinoff and Malyscheff[3] obtained its lead salt by the action of benzoyl chloride on lead sulfide. Klinger[4]

[1] This paper is an abstract from a Bachelor's Thesis presented to the Faculty of the University of North Carolina in June, 1928.

[2] Fleischer, *Ann.*, **140**, 241 (1866).

[3] Engelhardt, Latschinoff and Malyscheff, *Z. Chem.*, **1868**, 353; *Jahresb. über der Fortschritte der Chemie*, **1868**, 595.

[4] Klinger, *Ber.*, **15**, 862 (1882).

treated benzal chloride with potassium sulfhydrate. In 1902 Houben and Kesselkaul[5] announced the formation of the acid by the action of carbon disulfide on phenylmagnesium bromide. In 1906 Houben[6] described a series of arylcarbithioic acids.

In this paper is described the preparation of *p*-cymyl-2-carbithioic acid by the action of carbon disulfide on *p*-cymyl-2-magnesium bromide. From this acid various salts and esters were prepared.

The name given to the dithio acid follows the suggestion of Houben. The expression "dithiocarboxylic acid" indicates oxygen as well as sulfur and as there is no oxygen present such a designation should be avoided. The name given is made up of car (carbon), bi (two) and thio (sulfur) and seems to us to be a perfectly good and logical name.

Experimental Part

The Grignard Reagent.—2-Bromo-*p*-cymene was made by brominating cymene according to the method of Bogert and Tuttle.[7] The portion boiling at 103–105° at 5 mm. was used. Thirty g. of clean, dry magnesium turnings was washed with dry ether and covered with 500 cc. of dry ether. Several small crystals of iodine were allowed to dissolve at the bottom. In order to keep the iodine in contact with the magnesium the solution was not stirred while 250 cc. of bromocymene in 25cc. portions was added. The product was a grayish-black, somewhat sirupy liquid. It was decanted from the small residue of magnesium and used in this condition.

***p*-Cymyl-2-carbithioic Acid, $C_6H_3CH_3C_3H_7CSSH$.**—The Grignard reagent (the whole amount prepared above) was cooled by a freezing mixture to -10° and then 180 cc. of carbon disulfide was added dropwise and slowly enough to keep the temperature at -10°. This operation took three hours. Air was almost entirely excluded. After stirring had been continued for another hour, the stirring assembly was removed, the flask stoppered and the mixture kept cold by the freezing mixture for twelve hours. The reaction mixture was then poured upon a kilo of ice and hydrochloric acid was added until the liquid was acid to Congo Red. A reddish-orange ether layer separated out on top. This was removed with a separatory funnel. The aqueous layer was extracted three times with 200cc. portions of ether. The ether extracts were then combined and extracted with 150cc. portions of 5% sodium hydroxide solution until the alkali solution assumed only a slight yellow color or none at all. This gives a solution of the sodium salt of the carbithioic acid with some excess of alkali. This solution is used for making other salts. It does not keep well, decomposing in two to three days.

The free acid is obtained by covering the alkaline solution with ether and adding hydrochloric acid until acid to Congo Red. The free acid is then extracted with ether. It is a viscous red oil when its ether solution is evaporated in a vacuum. It does not solidify at -15°. It decomposes when an attempt is made to distil it at 2 mm. long before there is any evidence of boiling. The decomposition product is a thick brown oil of disagreeable odor. When the ether solution is allowed to evaporate in the air, a reddish-orange, gummy mass of slightly disagreeable odor remains. In ether solution the acid ranges from purple-red in concentrated solutions to orange in dilute solutions. The acid is fairly stable in ether solution, only slight decomposition being noticed

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[5] Houben and Kesselkaul, *Ber.*, **35**, 3696 (1902).

[6] Houben, *Ber.*, **39**, 3219 (1906).

[7] Bogert and Tuttle, This Journal, **38**, 1349 (1916).

after five months. The sodium, potassium, barium, strontium and calcium salts are soluble in water. The zinc salt is insoluble.

Zinc Salt of Cymylcarbithioic Acid, $(C_6H_3CH_3C_3H_7CSS)_2Zn$.—A solution of 5 g. of zinc chloride, 100 cc. of water and 15 cc. of glacial acetic acid was made. To this solution was added the freshly prepared solution of the sodium salt of the carbithioic acid, which contained some excess of sodium hydroxide, until no further precipitation took place. The precipitate was filtered off, dried and dissolved in absolute alcohol. The solution was boiled with animal charcoal and filtered. The cooled solution was poured into water, whereupon the zinc salt precipitated. It is an amorphous powder of yellow ochre color, soluble in alcohol, benzene, carbon tetrachloride and acetone but does not crystallize from any of them. It melts at 92°.

Anal. Calcd. for $C_{22}H_{26}S_4Zn$: S, 26.50; C, 54.7; H, 5.38; Zn, 13.52. Found: S, 26.39; C, 55.0; H, 5.43; Zn, 13.66.

Complex Salts

A number of salts were prepared in which the metal is half saturated with acetic acid and half with cymylcarbithioic acid. A metallic salt in dilute acetic acid solution is added to an aqueous solution of the sodium salt of the carbithioic acid. The precipitate is filtered and washed with a little alcohol to remove traces of resin. These salts dissolve in a number of organic solvents as alcohol, benzene, carbon tetrachloride and acetone, but they do not crystallize from them. The lead salt is brown and melts at 65°. The silver salt is a beautiful orange but it turns black in fifteen minutes. These were not analyzed.

Table I

Type Formula: $C_6H_3CH_3C_3H_7CSS\text{-}M\text{-}OCOCH_3$

Salt used	Color	Form	M. p., °C.
Zinc chloride	Yellow	Amorphous	196 decomp.
Copper sulfate	Red-yellow	Amorphous	75 decomp.
Mercuric chloride	Yellow	Amorphous	>300
Cadmium acetate	Yellow	Amorphous	125 decomp.

	Analyses							
	Carbon		Hydrogen		Sulfur		Metal	
Formula	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
$C_{13}H_{16}O_2S_2Zn$	46.8	47.1	4.81	4.86	19.22	18.95	...	...
$C_{13}H_{16}O_2S_2Cu$	47.2	46.9	4.83	4.89	19.33	19.56	19.62	19.84
$C_{13}H_{16}O_2S_2Hg$	33.3	33.12	3.41	3.40	13.64	14.03	...	...
$C_{13}H_{16}O_2S_2Cd$	41.0	40.9	4.61	4.63	16.79	16.96	...	...

Methyl Ester of Cymylcarbithioic Acid, $C_6H_3CH_3C_3H_7CSSCH_3$.—The ester is prepared by treating the aqueous solution of the sodium salt with dimethyl sulfate until a thick brown oil collects on the surface and a further addition causes no brown color in the aqueous layer. The sulfate is added slowly with stirring. The oil is separated, washed with dilute sodium hydroxide, then with water, dried over calcium chloride and distilled in vacuum. It is a sirupy liquid boiling at 167–168° and 8 mm. When pure it is not very disagreeable in odor. In dilute form it smells like a freshly cut turnip. It is quite stable. When exposed to the air for three days no change was noticed and it did not change in color in a sealed tube in the sunlight for a week.

Anal. Calcd. for $C_{12}H_{16}S_2$: S, 28.57; C, 64.3; H, 7.148. Found: S, 28.77; C, 64.1; H, 7.13.

Ethyl Ester.—Liquid boiling at 141–2° and 3 mm.

Anal. Calcd. for $C_{13}H_{18}S_2$: S, 26.97; C, 65.5; H, 7.57. Found: S, 26.88; C, 65.1; H, 7.53.

Action of Phenylhydrazine.—An unexpected reaction took place between phenylhydrazine and the carbithioic acid. Small, white plates were obtained, melting sharply at 112°. The substance was insoluble in most organic solvents and evolved hydrogen sulfide when heated with any such solvent. It contains 6.79% N and 16.18% S.

Acid Chloride.—The action of phosphorus pentachloride on the carbithioic acid gave a liquid boiling at 141° and 8 mm. Though its odor was somewhat sharp it gave no typical reaction with ammonia or aniline so doubt remains as to its nature.

Summary

1. *p*-Cymyl-2-carbithioic acid is obtained by the action of carbon disulfide on cymyl-2-magnesium bromide.

2. Its zinc salt was prepared.

3. Complex salts of metals with acetic acid and carbithioic acid were obtained. Zinc, copper, mercury and cadmium gave such salts.

4. The methyl and ethyl esters of carbithioic acid were prepared.

5. Reactions (undetermined) took place between the carbithioic acid and phenylhydrazine, also phosphorus pentachloride.

Chapel Hill, North Carolina

[Contribution from the Chemical Laboratory of the College of Liberal Arts of Northwestern University]

UNSYMMETRICAL ARSENO COMPOUNDS DERIVED FROM PARA-ARSONOPHENYLAMINO-ETHANOL AND PARA-ARSONOPHENYLGLYCINE-AMIDE[1]

By Charles Shattuck Palmer and Ernest B. Kester[2]

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During recent years there has been considerable interest in the attempts to apply *p*-arsonophenylglycine-amide in the form of its monosodium salt, "tryparsamide" (1), to the treatment of diseases of protozoal origin. Especial success has attended its introduction into the treatment of trypanosomiasis,[3] and it has also shown promise in paresis.[4] To a lesser

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[1] An abstract of Part I of a thesis submitted to the Graduate School of Northwestern University by Ernest B. Kester in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Research Fellow under grant from the Public Health Institute of Chicago.

[3] Jacobs and Heidelberger, This Journal, **41**, 1587 (1919); Brown and Pearce, *J. Exptl. Med.*, **30**, 417–496 (1919); Pearce, *ibid.*, **34**, supplement 1 (1921); Chesterman, *Trans. Roy. Soc. Trop. Med. Hyg.*, **16**, 394 (1923); Smillie, *J. Am. V. M. A.*, September, **1923**; Pearce, *J. Pharmacol.*, **25**, 159 (1925).

[4] Lorenz, Loevenhart, Bleckwenn and Hodges, *J. Am. Med. Assn.*, **80**, 1497 (1923); Moore, Robinson and Keidel, *ibid.*, **82**, 528 (1924); Lorenz, Loevenhart and Reitz, *Am. J. Med. Sci.*, **148**, 157 (1924); Lorenz, Loevenhart and Reese, *Z. Neur. Psych.*, **98**, 763 (1925); Loevenhart and Stratman-Thomas, *J. Pharmacol.*, **29**, 69 (1926).