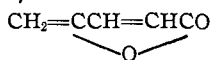


3. 3-Bromovinylacrylic acid absorbs one molecule of bromine in the 3,4-position to give 3,3',4-tribromo- $\Delta^1$ -pentic acid. Its structure was proved by ozonization.

4. An improved method for the preparation of vinylacrylic acid is given which doubles the best yield heretofore obtained.

5. On distillation 3,4-dibromo- $\Delta^1$ -pentic acid loses two molecules of hydrogen bromide to give a  $\gamma$ -lactone whose structure was proved to be



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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

## CARBITHIOIC ACID STUDIES. I. TOLYL-4-CARBITHIOIC ACID AND CERTAIN DERIVATIVES<sup>1</sup>

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There are three methods by which the carbithioic acids are usually made, namely, hydrolysis of the corresponding thio esters with alcoholic potassium hydroxide,<sup>2</sup> the action of carbon disulfide on benzene in the presence of anhydrous aluminum chloride<sup>3</sup> and the Grignard reaction.<sup>4,5</sup>

Sakurada<sup>2</sup> first isolated tolyl-4-carbithioic acid by the hydrolysis of ethyl dithio-*p*-toluate with alcoholic potassium hydroxide, the ethyl dithio-*p*-toluate being prepared by passing dry hydrogen sulfide into an ethereal solution of the corresponding thio-imino ester. However, none of its properties was studied and no derivatives were prepared other than the ethyl ester.

In this paper is described the preparation of tolyl-4-carbithioic acid by the action of carbon disulfide on tolyl-4-magnesium bromide. The acid is a viscous red oil having a disagreeable odor. Attempts to distil the acid resulted in decomposition. The sodium salt was more stable and was used in the preparation of the derivatives

Tolyl-4-carbithioic acid readily forms salts with the chlorides and acetates of inorganic metals. It is easily converted into thio esters by alkyl sulfates and alkyl halides. The thio esters are susceptible to ammonolysis, whereupon thio amides are obtained. In these respects the —CSSH group is similar to the —COOH group.

<sup>1</sup> This paper is an abstract of a thesis submitted in June, 1929, to the Faculty of the University of North Carolina by W. J. Mattox in candidacy for the degree of Master of Arts.

<sup>2</sup> Sakurada, *Mem. Coll. Sci. Kyoto*, **10**, 79-83 (1926).

<sup>3</sup> Jörg, *Ber.*, **60**, 1466 (1927).

<sup>4</sup> Houben, *ibid.*, **39**, 3219 (1906).

<sup>5</sup> Wheeler and Thomas, *THIS JOURNAL*, **50**, 3106 (1928).

The acid differs from the carboxylic acids in that the —CSSH group is converted by oxidizing agents such as nitric acid and permanganate into the —COOH group. Attempts to prepare an acid chloride were negative.

### Experimental Part

**Tolyl-4-magnesium Bromide.**—Thirteen grams of clean, dry magnesium shavings was placed in a liter balloon flask provided with a reflux condenser and a mixture of 200 ml. of absolute ether and 25 g. of *p*-bromotoluene added. A small crystal of iodine was allowed to dissolve on the bottom. The reaction usually started in a few minutes. *p*-Bromotoluene was then added in 10-ml. portions until 85 g. had been added. After the reaction was complete, the ether solution was decanted into a dry flask.

**Tolyl-4-carbithioic Acid.**—The flask containing the Grignard reagent was surrounded by a freezing mixture and cooled to 0°; 38 g. of carbon disulfide was added dropwise so that the temperature did not rise above 0°. This required about an hour. Precautions were taken to exclude all moisture. After all of the carbon disulfide had been added the stirring was continued for about three hours. The ice-bath was removed and the reaction product allowed to stand at room temperature for an hour or longer. The solution was poured into 500 g. of ice and dilute hydrochloric acid then added to dissolve the magnesium hydroxide. The deep red ether layer was removed by means of a separatory funnel and extracted with 100-ml. portions of 5% sodium hydroxide until the latter was only slightly colored. This aqueous solution of the sodium salt was covered with 200 ml. of ether and dilute hydrochloric acid added until the aqueous solution was slightly acid. The free acid which was then in solution in the ether was washed well with water. From three to four precipitations from the aqueous solution of the sodium salt were necessary to purify the acid. The ether was evaporated in a desiccator to obtain the free acid.

Tolyl-4-carbithioic acid is a dark red, viscous oil having a disagreeable odor. All attempts to distil it, even at 3-mm. pressure, resulted in decomposition. It solidifies at 27° into a mass of dark red crystals. It is very soluble in benzene, toluene, ether and acetone, slightly soluble in alcohol, carbon tetrachloride and chloroform and insoluble in water. The acid decomposes slowly on exposure to the atmosphere, but is much more stable in ether solution.

**Zinc Salt of Tolyl-4-carbithioic Acid.**—Five grams of zinc acetate dissolved in 150 ml. of water was added to 15 ml. of acetic acid. To this solution was slowly added, with stirring, a slight excess of the sodium salt of the acid and the stirring continued for three to four hours. It is necessary to keep the sodium salt in excess as otherwise complex products are formed. After the precipitate was washed and dried, the zinc salt was twice extracted with hot absolute alcohol. It is soluble in benzene, toluene and hot alcohol.

**Lead Salt of Tolyl-4-carbithioic Acid.**—This salt was prepared similarly to the zinc salt. It is practically insoluble in all the organic solvents.

**Methyl Ester of Tolyl-4-carbithioic Acid.**—An aqueous solution of the sodium salt was treated with dimethyl sulfate, with shaking, until a dark red oil separated out and the red color had disappeared from the aqueous layer. The mixture was gently refluxed for thirty minutes to insure complete reaction. The ester was extracted with ether, the ethereal solution washed with water, dried and distilled in vacuum. It is a dark red oil having a disagreeable odor.

**Ethyl Ester.**—This ester was prepared similarly to the methyl ester, using the corresponding alkyl sulfate. It resembles the methyl ester in its physical properties.

***n*-Butyl Ester.**—Ninety-five grams of the sodium salt of the acid dissolved in 300

ml. of water and 70 g. of *n*-butyl bromide were refluxed until a red oily layer separated out and the aqueous layer was colorless. When cooled, the ester was extracted with ether, washed, dried and distilled in vacuum. It is a red oily liquid of disagreeable odor and solidifies at 20°.

*p*-Nitrobenzyl Ester.—To 4 g. of *p*-nitrobenzyl bromide dissolved in 40 ml. of hot alcohol was slowly added, with stirring, a freshly prepared aqueous solution of the sodium salt in slight excess. Gentle boiling was continued for five minutes. After cooling the dilute alcohol was decanted off the thick oil which separated out. The oil was washed with 95% alcohol and placed on a porous plate to crystallize. The crude ester was purified by dissolving in hot absolute alcohol and heating with several portions of charcoal. The filtrate upon cooling yielded large red rectangular plates in the form of clusters. The ester is soluble in ether, hot toluene, alcohol and benzene.

Amide of Toly1-4-carbithioic Acid.—Seven grams of the methyl ester and 20 ml. of concentrated ammonium hydroxide were placed in a 50-ml. glass-stoppered bottle for five or six days. The bottle was shaken occasionally during this time. The crude amide which separated out, was filtered off, washed with petroleum ether and crystallized from hot toluene. It is soluble in ether, hot alcohol and benzene. Methyl mercaptan is also formed in the reaction.

*p*-Toluide of Toly1-4-carbithioic Acid.—Ten grams of *p*-toluidine, 6 g. of the dry sodium salt and 6 ml. of concentrated hydrochloric acid were placed in a small beaker and gently heated for thirty minutes. The product was cooled and extracted with 50 ml. of hot toluene. The toluene solution was boiled with several portions of charcoal, filtered and set aside to crystallize. Long yellow needles separated out when about one-third of the toluene had evaporated. It is soluble in hot alcohol, benzene and toluene.

Oxidation of Toly1-4-carbithioic Acid.—To an ether solution of the acid cooled to 0° was added nitric acid (sp. gr. 1.42) dropwise, with stirring, until the red color of the acid changed to a light yellow. The mixture was removed from the ice-bath and stirring continued for an hour. The oxidation product was extracted with ether, purified through its sodium salt and finally recrystallized from dilute alcohol. The white crystalline product melted at 181°. Qualitative tests for sulfur were negative. Molecular-weight determinations and other tests proved the oxidation product to be *p*-toluic acid. Similar results were obtained with potassium permanganate at room temperature. At higher temperatures complex products are obtained.

Action of Phosphorus Pentachloride on Toly1-4-carbithioic Acid.—Phosphorus pentachloride reacts with the acid, producing a viscous red liquid. All attempts to distil the product in a vacuum resulted in decomposition. Phosphorus trichloride and phosphorus oxychloride were used and similar results obtained.

TABLE I  
DATA ON DERIVATIVES

No.	Compound	Color	Form	Solvent	M. p., °C.
1	Zinc salt	Light red	Amorphous	Hot abs. alcohol	180
2	Lead salt	Brick-red	Amorphous	None	200 (decomp.)
3	Amide	Lemon-yellow	Needles	Hot toluene	155
4	Toluide	Yellow	Needles	Hot toluene	170.5
5	<i>p</i> -Nitrobenzyl ester	Red	Plates	Hot abs. alcohol	70.5
				Sp. gr., at 30°	B. p., °C.
6	Methyl ester	Red	.....	....	130 (3 mm.)
7	Ethyl ester	Red	.....	1.1173	132 (3 mm.)
8	<i>n</i> -Butyl ester	Red	.....	1.0700	169 (5 mm.)

TABLE II  
ANALYSES

No.	Formula	Carbon		Hydrogen		Sulfur		Metal	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1	$C_{16}H_{14}S_4Zn$	48.03	48.08	3.53	3.66	32.08	32.14	16.36	16.22
2	$C_{16}H_{14}S_4Pb$	35.45	35.80	2.60	2.70	23.68	23.94	38.26	38.18
3	$C_8H_9NS$	63.51	63.95	6.00	6.13	21.21	21.17		
4	$C_{16}H_{16}NS$	74.62	74.73	6.26	6.37	13.29	13.39		
5	$C_{16}H_{16}O_2NS_2$	59.35	59.61	4.32	4.46	21.14	20.99		
6	$C_9H_{10}S_2$	59.27	58.75	5.53	5.65	35.19	35.14		
7	$C_{10}H_{12}S_2$	61.15	60.64	6.16	6.16	32.68	32.65		
8	$C_{10}H_{10}S_2$	64.21	63.60	7.19	7.37	28.59	28.71		

## Summary

1. Toly-4-carbithioic acid was prepared by the action of carbon disulfide on tolyl-4-magnesium bromide.
2. The acid readily forms salts and esters.
3. A thio amide and the *p*-toluide were prepared.
4. The acid is very sensitive to oxidizing agents.
5. Attempts to prepare the acid chloride were negative.

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## THE EFFECT OF HEAT UPON CROTONIC ACID

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In the course of a study of the mutual solubility relations of geometrical isomers, an unsuccessful attempt was made to prepare isocrotonic acid by a method based upon the work of Michael<sup>2</sup> and Schulthess and of Morrell and Hanson.<sup>3</sup> According to these investigators the product obtained upon heating crotonic acid or isocrotonic acid to a temperature above 100° is a binary mixture of these two acids. The latter authors made a more extensive study of the system and came to the conclusion that it afforded an example of "unstable" or "false equilibrium." Since there is considerable doubt whether such cases actually exist,<sup>4</sup> the system promised to be interesting from this point of view also.

Morrell and Hanson obtained their "equilibrium" values by heating a sample of each acid for successive six-hour periods at various temperatures and determining the primary freezing points of the solutions obtained at each temperature. (Their data are included in Table I.) The composition

<sup>1</sup> Du Pont Fellow, 1924-1925.<sup>2</sup> Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 236 (1892).<sup>3</sup> Morrell and Hanson, *Chem. News*, **90**, 166 (1904); *J. Chem. Soc.*, **85**, 1520 (1904).<sup>4</sup> See Roozeboom, "Die Heterogenen Gleichgewichte," **1918**, Vol. II, Part 3, p. 13; Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 17.